Novel Phosphorus Heterocycles

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NOVEL PHOSPHORUS HETEROCYCLES

From Rings to Cages

Sander George Adriaan van Assema

2007

VRIJE UNIVERSITEIT

Novel Phosphorus Heterocycles
From Rings to Cages

ACADEMISCH PROEFSCHRIFT

ter verkrijging van de graad Doctor aan
de Vrije Universiteit Amsterdam,
op gezag van de rector magnificus
prof.dr. L.M. Bouter,
in het openbaar te verdedigen
ten overstaan van de promotiecommissie
van de faculteit der Exacte Wetenschappen
op woensdag 6 juni 2007 om 13.45 uur
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De Boelelaan 1105

door

Sander George Adriaan van Assema

geboren te Rotterdam

promotor: prof.dr. K. Lammertsma
copromotor: dr. M. Schakel

aan mijn ouders

Love hides in molecular structures

("Love Hides" From the album "ABSOLUTELY LIVE"
The Doors 1970, Jim Morrison (1943-1971)

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Chapter 1

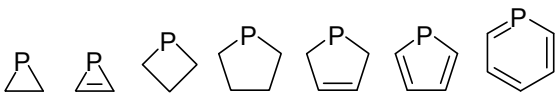
Introduction

In this introduction, a literature overview is given of the synthesis of phosphacycles and -cages. Incorporating phosphorus in carbon frameworks can lead to novel compounds with potential applications as ligands in catalysis or as new materials. Development of useful building blocks is therefore of prime importance. This overview introduces various methods for the synthesis of building blocks and cages, followed by a brief outline of the research presented in this thesis.

In the area of molecular frames two aspects are addressed in this introduction. The first section gives an overview on cycles and cages that contain phosphorus atoms in unusual settings like polycyclic rings that may be suitable for the synthesis of novel ligands for various transition metal complexes. The second section concerns the incorporation of phosphorus in acetylenic scaffolds. The use of silicon or metals in the synthesis of such scaffolds is also briefly described, but the all-carbon acetylenic scaffolds are not included as they have been extensively reviewed elsewhere.[1]

1.1 Basic Phosphorus Heterocycles

Phosphorus containing heterocycles are abundant in the literature and are present in the most exotic forms. The smallest rings, the phosphirane **1** and phosphirene **2**, have been the focus of our research group over the past 10 years. The 4-membered phosphetanes **3** and phosphetes are becoming increasingly popular as chiral ligand systems. The most common members of the family of cyclic phosphines are the 5-membered phospholanes **4**, phospholenes **5** and phospholes **6**. Larger ring systems are becoming increasingly more important, such as the aromatic phosphinines (**7**).[2]



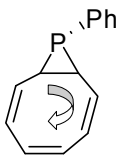
1 **2** **3** **4** **5** **6** **7**

The chemistry of heterocyclic phosphorus compounds has been extensively reviewed in *Phosphorus-Carbon Heterocyclic Chemistry: The Rise of a New Domain*; Ed. F. Mathey, Pergamon, Oxford, **2001**. The next sections will discuss relevant literature concerning the topics of this thesis.

1.2 Polycyclic P-Heterocycles via Phosphinidenes

An important reactive intermediate suitable for synthesizing phosphorus heterocycles is the low-valent phosphinidene [R-P], which is the phosphorus analogue of the well-known carbene [R_2C:]. Electrophilic phosphinidenes, generated from various precursors,[3] can add to C=C and C≡C bonds thereby forming phosphiranes **1** and phosphirenes **2**, respectively. Interesting polycyclic compounds can be obtained from *inter*molecular and *intra*molecular addition reactions to unsaturated substrates.

Reaction of the cyclooctatriene dianion with dichlorophenylphosphine was shown to give exclusively phosphirane **8**,[4a] in which the PPh group *walks* in a series of 1,7-sigmatropic shifts around the hydrocarbon ring in solution at room temperature. Because of the inversion of the phosphorus atom at each step the phenyl group remains in an *anti*-orientation.



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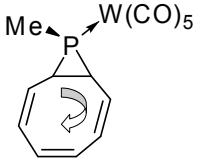
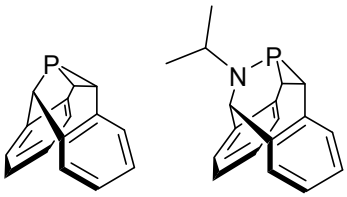


9

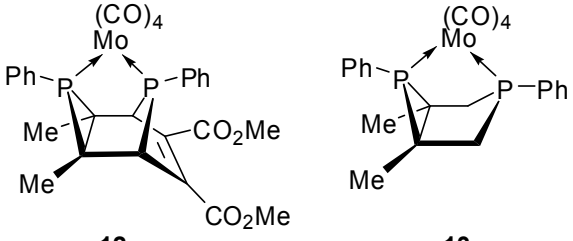
A similar walk-rearrangement is observed for the *anti*-isomer **9** that is obtained from the addition of MeP-$W(CO)_5$ to cyclooctatetraene.[4b]

In related *intra*molecular cycloadditions, Grützmacher *et al.* synthesized polycyclic phosphasemibullvalene **10**[5] and BABAR-phos **11**[6]; the plausible phosphinidene intermediate could not be trapped intermolecularly by other substrates. BABAR-phos has demonstrated its potential as a valuable ligand for transition metal complexes in homogeneous catalysis.[7]



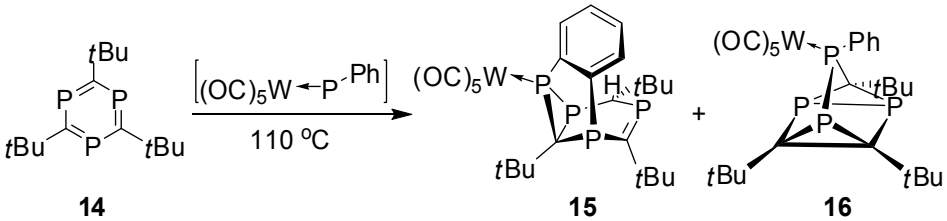
10 **11**

Lammertsma *et al.* have reported the synthesis of diphos baskets from the *intra*molecular phosphinidene addition, generated from a 7-phospha-norbornadiene unit, to a 7-phosphanorbornadiene or phospholene ligand complexed to a $Mo(CO)_4R$ group.[8] Cage compounds **12** and **13** resulted from the connection of the two phosphorus atoms by a bridging Mo atom.



12 **13**

Also investigated was the *inter*molecular phosphinidene addition to 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene,[9] which resulted in the unexpected formation of products **15** and **16**. (Scheme 1).

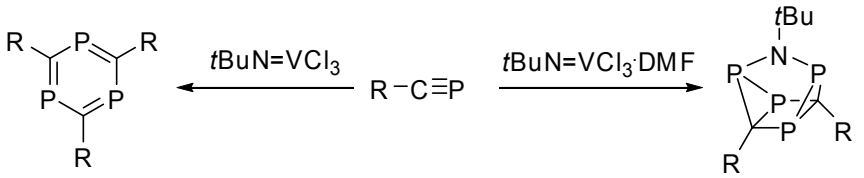


14 **15** **16**

Scheme 1 Phosphinidene addition to triphosphabenzene **14**

1.3 Cycles and cages from R-C≡P

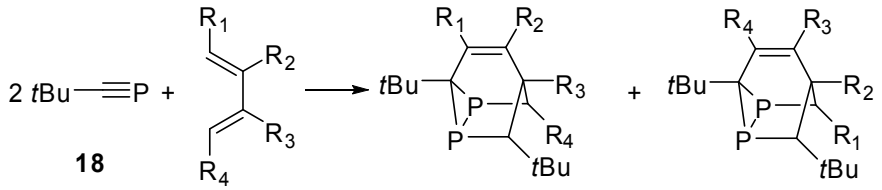
Phosphaalkynes have been very effective reactants in the synthesis of unusual polycyclic rings and cages. With *t*BuN=VCl_3 as catalyst, R-C≡P reacts to give triphosphabenzene derivatives, like **14**, with various alkyl substituents on carbon. Interestingly, when the catalyst is complexed with DMF, i.e., *t*BuN=VCl_3·DMF, quadricyclane structures (**17**) are formed.[10]



14 **17**

Scheme 2. Possible reactions with phosphaalkynes

Two molecules of phosphaalkyne **18** react with 1,3-dienes in a sequence of [4+2]-, ene- and *intra*molecular [4+2] reactions to give two diphosphatricyclic compounds **19** and **20** with a diphosphirane unit (Scheme 3).[11]

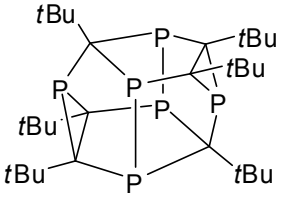


18 **19** **20**

Scheme 3. Reaction of phosphaalkyne with a 1,3-diene

A hexamer of *t*-butylphosphaalkyne, namely **21**, has been synthesized as one of the organophosphorus products that result from the reaction of a mixture of $P_3C_2(tBu)_2^-$ and $P_2C_3(tBu)_3^-$ with $PtCl_2$(cod) (cod = 1,5-

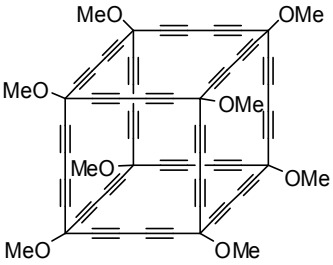
cyclooctadiene).[12] **21** can be considered as a dimer of valence isomeric triphosphabenzene.



21

1.4 Cycles from ethynylphosphines (RP-(C≡CH)$_2$)

Another possible route toward cycles and cages with embedded phosphorus atoms starts with ethynylphosphines. Many groups have demonstrated that acetylene scaffolds may lead to unusual and interesting structures like **22**.[13]

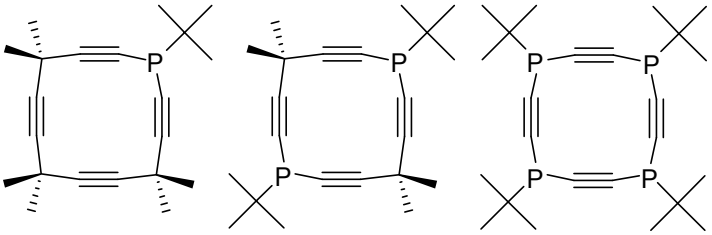


22

1.4.1 Phosphines with an acetylene linkage

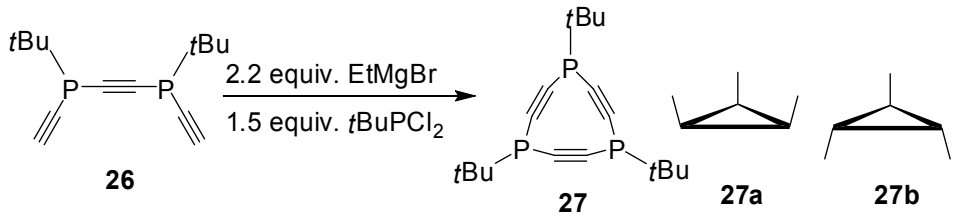
The use of phosphorus in the synthesis in carbon frameworks is limited to a few examples. Alkynyl conjugated organophosphorus compounds were first synthesized by Scott *et al.* in 1990.[14] A series of phospha[n]pericyclynes (**23**-**25**) were prepared consisting of a cyclic arrangement of acetylene units with saturated carbon and/or phosphorus corners. The numeral prefix [n] is used to indicate both the numbers of corners and sides. The larger [6] and [8]pericyclynes were also prepared by

the same group. All these phospha[n]pericyclynes are prone to oxidation by air.



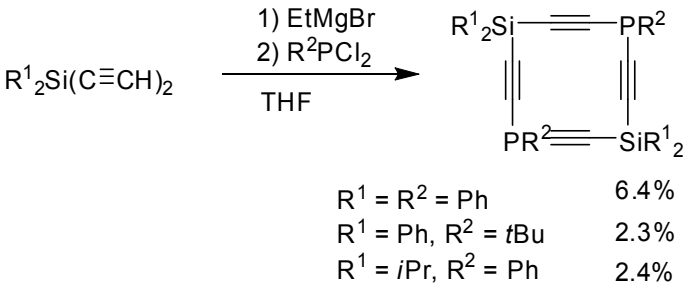
23 **24** **25**

These heterocycles differ from the all carbon analogues, because diastereomers can be expected as a result of the high barrier for pyramidal inversion of phosphorus. [15] This means that **24** and **25** exist as two and four non-interconverting diastereomers, respectively. Compound **25** has been prepared in a one step 'shotgun' synthesis by coupling of the appropriate acetylenic Grignard derivative with *tert*-butyldichlorophosphine (*t*BuPCl$_2$). Despite its inherent simplicity, the low product selectivity and difficult separation of isomers leads to low isolated yields and therefore hampers their access. The smallest possible triphosphapericyclyne **27** has been synthesized via cyclization of **26** with *t*BuPCl$_2$ in 16% yield (Scheme 4).[14a] Interestingly, only one (**27b**) of the two possible isomers was formed; the all-*cis* isomer **27a** is not detected by ^{31}P NMR, possibly due to much steric hindrance between the three *t*Bu-groups.



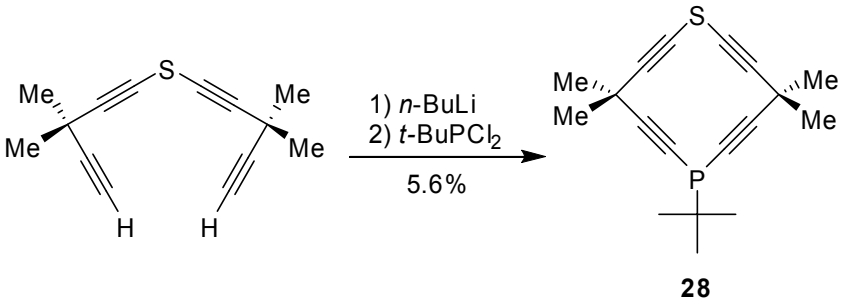
Scheme 4. Synthesis of triphospha[3]pericyclyne

In a similar strategy, twelve-membered cyclic diethynylphosphine derivatives with embedded silane groups have been synthesized bearing reactive acetylene and silane moieties.[16] Treatment of diethynylsilanes with 2 equivalents of EtMgBr in THF, followed by the reaction with the appropriate dichlorophosphines reportedly results in the formation of the cyclic compounds in yields up to 6.4% depending on the substituents on silicon and phosphorus (Scheme 5). Despite the low yield and polymeric by-products, the desired ring systems could be isolated by gel permeation chromatography. The product ratios depend on the phosphine substitution pattern. These strained ring systems were shown to be surprisingly air-stable and did not convert to phosphine oxides.



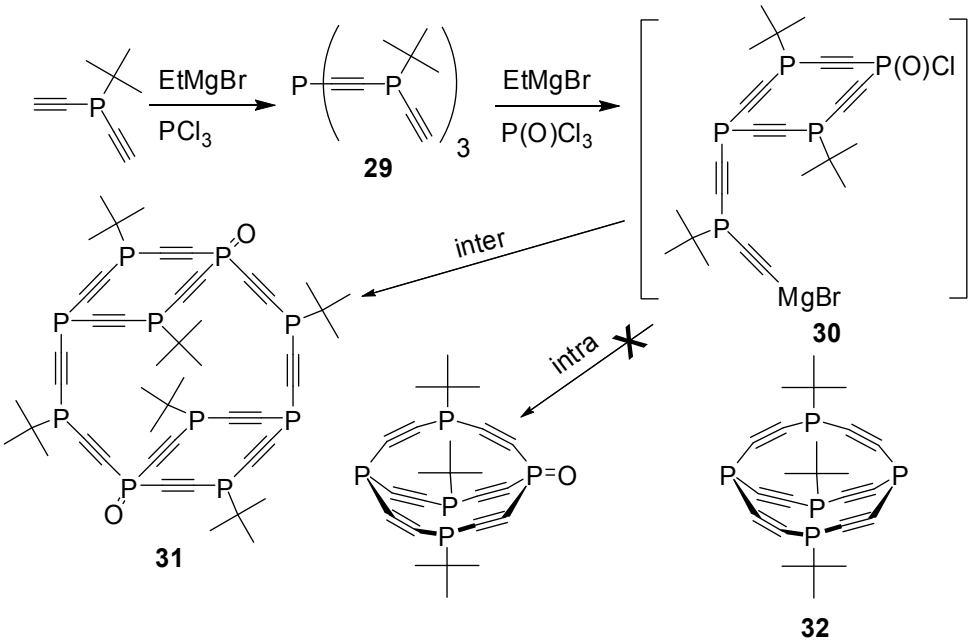
Scheme 5. Synthesis of mixed Si/P-pericyclynes

The P/S derivative of [4]pericyclyne **28** (Scheme 6) likewise did not show any tendency to oxidize in air either.[14b] The stability toward oxidation of these mixed [4]pericyclynes is in sharp contrast to all the other phospha[N]pericyclynes reported so far.



Scheme 6. Synthesis of a mixed P/S-[4]pericyclyne

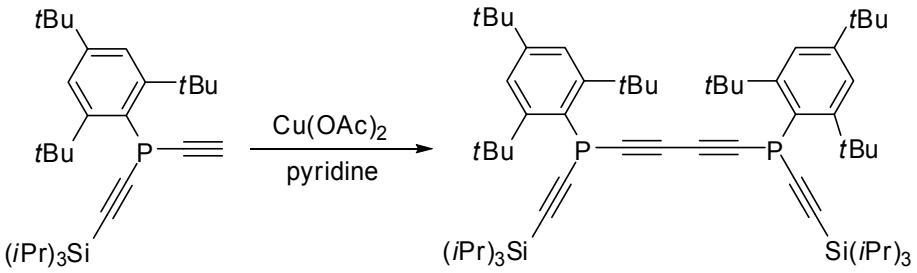
Scott *et al.* tried to extend the synthesis of phosphapericyclynes to three dimensional structures.[14b] Bicyclic tetraphosphine **32** was selected as an initial target for the *intra*molecular cyclization of presumed reactive intermediate **30**, but could not be isolated. Instead, cage compound **31** was isolated from reaction of **29** with $P(O)Cl_3$ and is the apparent dimer of **30**, formed by a double *inter*molecular Grignard reaction (Scheme 7).



Scheme 7. Attempted synthesis of cages from ethynylphosphines

1.4.2 Phosphines with a butadiyne linkage

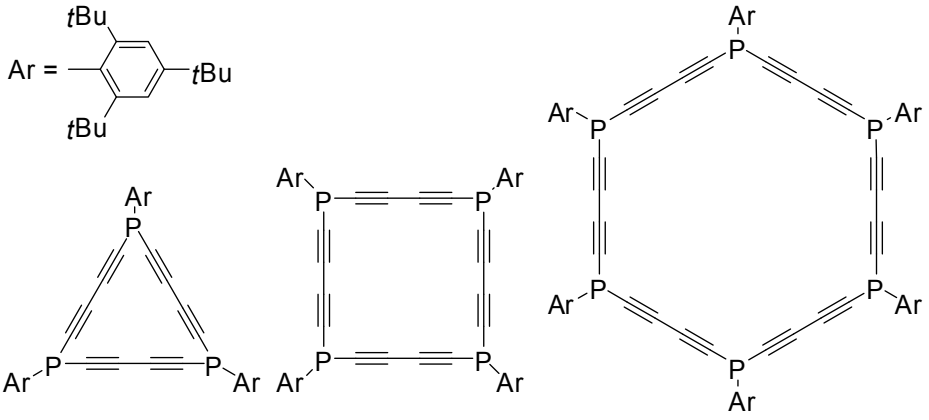
Märkl and co-workers extended the field of ethynylphosphines in a different direction.[17] They used various acetylene coupling reactions and multistep procedures to synthesize polyphosphines with 1,3-butadiyne linkages from open-chain polyphosphapolyynes and the phospha-macrocycles were obtained by *intra* or *inter*molecular coupling. The so-called polyphospha[m]cyclo[n]carbons, with (m+n) = 15, 20, 25, 30, 40) can be considered as precursors for cyclic P_mC_n systems. A particularly interesting observation was made for building block **34**, synthesized from **33** via an Eglinton-coupling.[17]



33 **34**

Scheme 8. Eglinton coupling of an ethynylphosphine

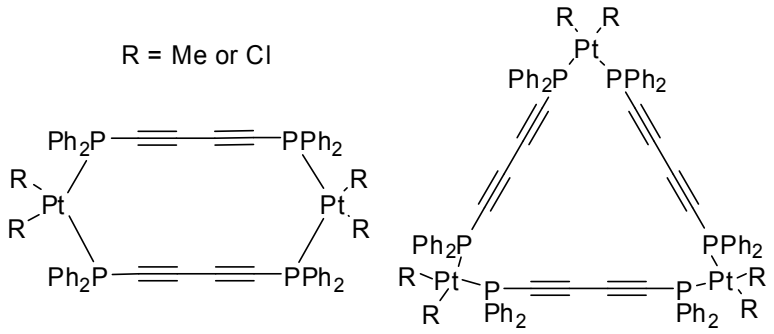
Its $^{31}P\{^1H\}$ NMR spectrum showed 2 resonances (-66.53 ppm and -66.29 ppm) at 21 °C that coalesced at 35.1 °C, which was explained by inversion of the phosphine centers of the diastereomeric *meso* and *racemic* forms. Further coupling reactions yielded the 15-, 20-, and 30-membered ring structures **35**, **36** and **37**, respectively.



35 **36** **37**

These products are all stable compounds due to the large supermesityl (2,4,6-tri-*tert*-butylphenyl) group on phosphorus that shields the reactive centers from oxygen and other reagents.

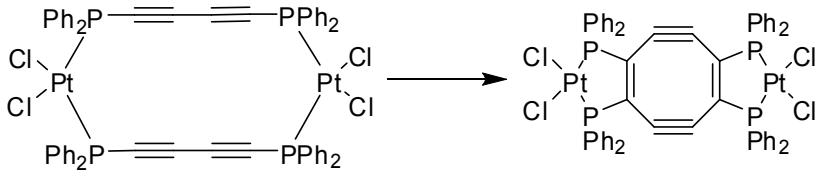
Cyclic structures have also been formed by linking diphosphabutadiyne units by transition metal groups. For example, reaction of $[Pt(CH_3)_2(COD)]$ or $[PtCl_2(COD)]$ with bis(diphenylphosphino)-butadiyne resulted in a mixture of bridged dimer **38** and trimer **39**.[18]



38 **39**

The metal center acts as a template in this reaction and brings the phosphine units together. Interestingly, the $PtCl_2$ complexes are thermally not stable and compound **38** rearranges at room temperature via a formal

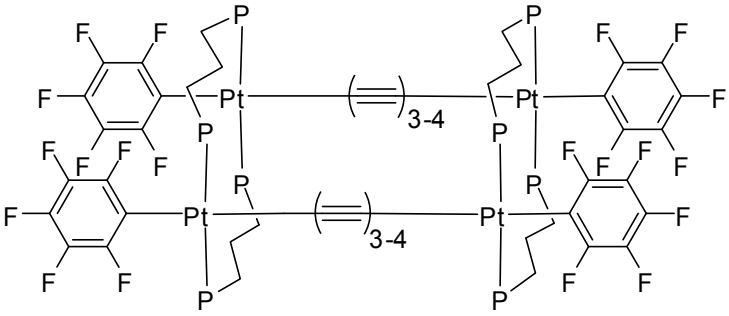
[4+4] cycloaddition to 8-membered ring **40** (Scheme 9). A related rearrangement was observed for **39**.

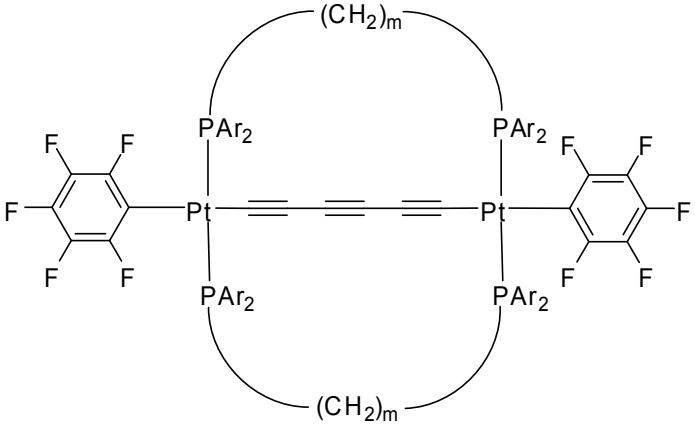


38 **40**

Scheme 9. Rearrangement of $PtCl_2$ complex **38**

Transition metal groups with phosphorus have also been used to link sp-hybridized carbon chains to obtain metal capped polyynediyl chains and cycles. Exemplary are studies by Gladysz *et al.*, who used oxidative Hay coupling conditions to synthesize Pt-capped carbon chains (Scheme 10).[19] The P-atoms in these molecules are used to link different chains and form, for example, molecular bundles[20] or wires[21]. Metal capped polyynediyl chains may be used in the field of molecular electronics. Compounds with polyynediyl moieties have been used as connectors in sophisticated molecular assemblies.[22]

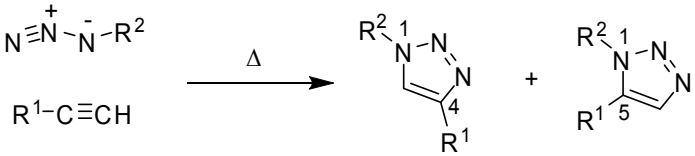




Scheme 10. Platinum polyynediyl complexes

1.5 P-Acetylenes in cycloaddition reactions with azides

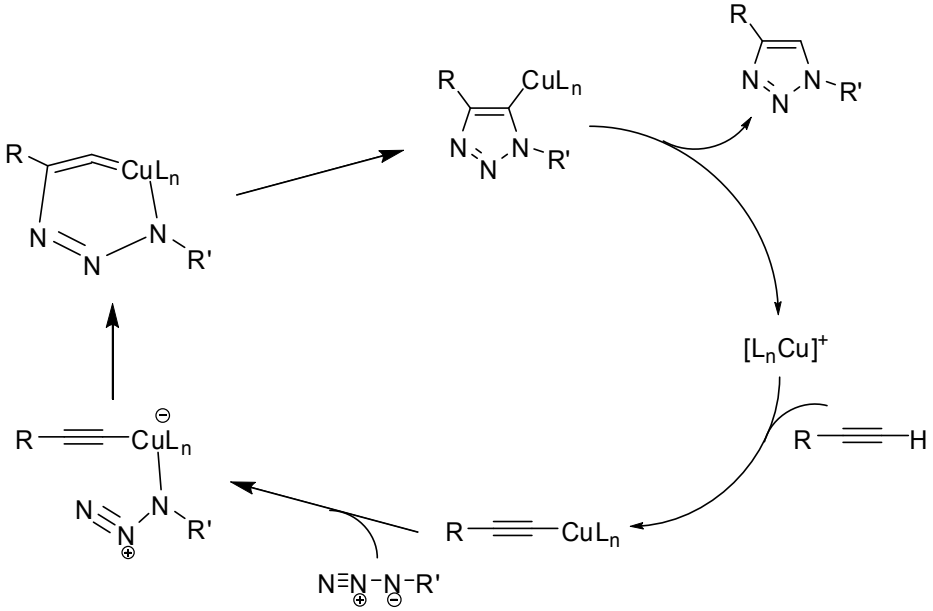
Besides the synthesis of P/C-chains, rings, and cages by linking acetylenic phosphines, the acetylene part of P-alkyne itself can be used as a molecular building block. The Huisgen 1,3-dipolar cycloaddition constitutes such an example. This reaction is popularly known as the 'click-reaction', and combines an alkyne with an azide to generate the very stable triazoles.[23]



Scheme 11. 1,3-dipolar cycloaddition with an azide and an alkyne

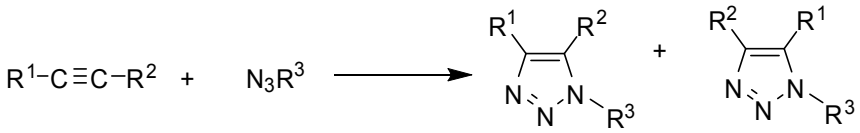
In 2002, a catalytic version of this reaction was discovered leading to a tremendous activity in this field.[24] Cu(I) is used as catalyst and has the added advantage that only the 1,4-disubstituted 1,2,3-triazole is generated from a terminal alkyne. The mechanism of this reaction has been

studied experimentally[25a] and computationally[25b] and is shown in a simplified manner in Scheme 12.



Scheme 12. Catalytic cycle for Cu(I)-catalyzed click-reaction

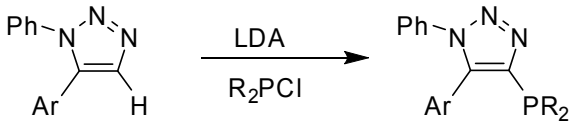
The need for a terminal alkyne in this catalytic reaction suggests the prensence of a Cu-acetylide intermediate. Coordination of the copper atom to one of the nitrogen atoms followed by cyclization leads to the experimentally found 1,4-isomer. The use of phosphorus substituted alkynes in the synthesis of triazoles is very limited. Only a few examples of the thermal cycloaddition reaction have been reported that yielded, as expected, the two possible isomers.[26]



a $R^1 = P(O)(OEt)_2$; $R^2 = CO_2Et$; $R^3 = CH_2CO_2Me$ (4) ratios (7)
b $R^1 = PMe(O)(OEt)$; $R^2 = H$; $R^3 = CH_2CO_2{}^tBu$ (3) (1)

Scheme 13. Cycloaddition of phosphorus substituted alkyne with azides

The synthesis of 1,5-disubstituted triazoles with a monophosphine substituent and their use as ligands for catalysis have been reported by Zhang *et al.*[27] These ligands, named ClickPhos (**42**), were however not directly synthesized from a phosphorus substituted alkyne, but instead from the 1,5-disubstituted triazole **41**, generated selectively using the procedure by Sharpless *et al.*[28], by deprotonation with LDA and subsequent reaction with chlorophosphines.

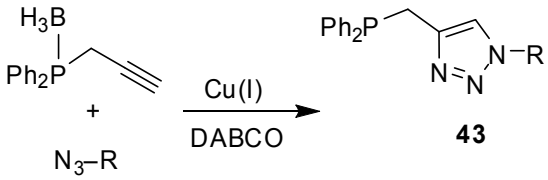


41 **42**

Ar = Ph, 1-Np, 2-OMePh
R = Ph, Cy, tBu

Scheme 14. Synthesis of ClickPhos ligands

Recently, a novel P,N-type ligand family **43** (ClickPhine) was also developed from the click reaction of alkynes bearing a BH_3 protected phosphine with various azides giving rise to heterogeneous and homogeneous catalysts effective in Pd-catalyzed allylic alkylation reactions.[29]



43

R = Ar, Alk, Polystyrene, Dendrimer

Scheme 15. Synthesis of ClickPhine ligands

1.6 Scope and Outline of this Thesis

The main objective of the research described in this thesis was to explore the synthesis of novel compound classes with phosphorus embedded in the molecular frame. These new compounds can be obtained as (a) ligand-systems generated by means of phosphinidene addition to unsaturated bonds or by cyclization reactions or (b) by linking phosphines and alkynes in linear or cyclic arrays. The synthesis and reactions of various novel building blocks are described.

Chapter 2 describes the synthesis of three novel bidentate diphos baskets via an *intra*molecular phosphinidene addition. The two phosphorus atoms are joined via a Mo metal and carbon, nitrogen or oxygen substituted backbones are used. Crystal structures of the baskets with the nitrogen and oxygen backbone are presented and discussed.

In ***Chapter 3***, we describe the decomplexation of phosphirene and phosphirane $Mo(CO)_4(PMe_3)$ complexes. Due to the additional trimethylphosphine ligand, the complexes are synthesized at mild temperatures compared to other $Mo(CO)_5$-complexed phosphinidene addition products and can be demetallated under CO pressure.

In ***Chapter 4*** we explore the synthesis of cyclic phosphines with acetylenic substituents. The phosphorus group is protected with an oxygen atom and the synthesis of several novel building blocks is described. Cyclized products with a single acetylene linkage are obtained from Grignard reactions and products with a butadiyne linkage are the result from coupling reactions under oxidative Hay conditions.

Chapter 5 discusses the application of phosphine substituted alkynes in the synthesis of novel phosphine and nitrogen ligands. A Cu(I)-catalyzed click reaction with phenylazide results in different phosphine substituted 1,2,3-triazoles. We report the N-Rh complex, the P-W complex and a bimetallic N-Fe/P-W complex.

Chapter 6 deals with the synthesis of P-alkyne building blocks. In contrast to the research presented in Chapter 3, these compounds are not protected with an oxygen atom and they show very different reactivities. An amino-group on phosphorus is used to selectively introduce different acetylenes.

1.7 References

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Chapter 2

Bidentate Phosphorus Baskets via Intramolecular Phosphinidene Addition

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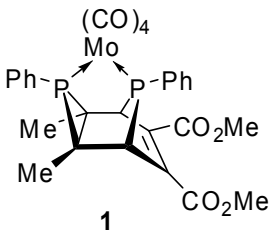
2.1 Abstract

Intramolecular phosphinidene addition to the C=C bond of Mo-complexed 7-membered phosphorus heterocycles affords three novel diphos $Mo(CO)_4$ complexes (**18-20**). The three bidentate phosphorus baskets differ in the composition of the 7-membered ring in which one phosphorus atom is flanked by CH_2, NCH_3, or O groups. The unsaturated tetrahydrophosphepine precursors are synthesized by either ring closing metathesis (C- and N-derivatives) or by a cyclization sequence (O-derivative). The crystal structures of the nitrogen (**19**) and oxygen (**20**) containing baskets have relatively small P-Mo-P angles of 76.240(13) and 77.626(12)°, respectively. Complex **20** has slightly shortened Mo-P bond lengths.

2.2 Introduction

Transition metal complexes with polycyclic bidentate phosphine ligands are rare. They are of interest because of the structural rigidity of the ligand that can affect both the access to and the electronic properties of the transition metal, which are aspects relevant to the design of catalysts. Two such molybdenum complexes are known, **1** with a tricyclic ligand and **2** with a bicyclic ligand.[1] Their phosphorus atoms are separated by two C_2-bridges. The crystal structure of **2** has an extremely small P-Mo-P bond angle of 69.732(16)°. Both these highly stable complexes have a chelating phosphirane ring. They were synthesized by *intra*molecular cycloaddition of a transient phosphinidene ($RPML_n$) to the double bond of the 5-membered phosphole ring (L) using the transition metal (cis-$RPMo(CO)_4L$) as template. Mathey et al[2] used a related double *inter*molecular cycloaddition (to cyclooctene) for the synthesis of **3**. Grützmacher's BABAR-Phos **4**,[3] another polycyclic ligand with a phosphirane ring, has demonstrated its potential in catalysis. This very

stable ligand has the advantage of being reformed from the metallaphosphetane, which otherwise usually leads to loss of catalyst.[4]



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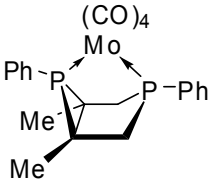

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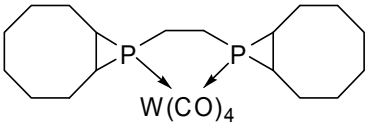

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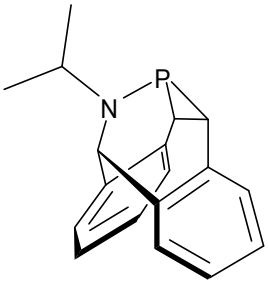

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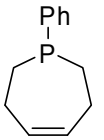
In the present study we report new molybdenum complexes with larger sized polycyclic bidentate phosphorus ligands that include N- and O-atoms embedded into the hydrocarbon frame that separates the phosphorus atoms. As starting point we use the P-phenyl derivatives of the 7-membered rings (L), 2,3,6,7-tetrahydro-1*H*-phosphepine **5,** 1,3-dimethyl-2,3,4,7-tetrahydro-1*H*-1,3,2-diazophosphepine **6**, and 4,7-dihydro-1,3,2-dioxaphosphepine **7**. The strategy is to ligate the ring in a *cis*-fashion in $PMo(CO)_4L$ and convert the P-ligand to a terminal phosphinidene complex for *intra*molecular cycloaddition to the olefinic bond of the 7-membered ring (L) to build the new 'baskets' **18**, **19** and **20**. Relevant to the synthesis is whether the cycloaddition is influenced by the ring size of ligand L and whether heteroatoms will influence this process, for example, by competing ylide formation.



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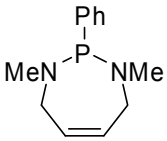

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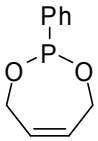

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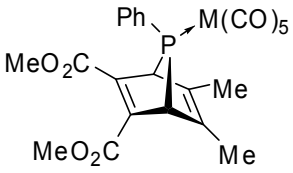
2.3 Results and Discussion

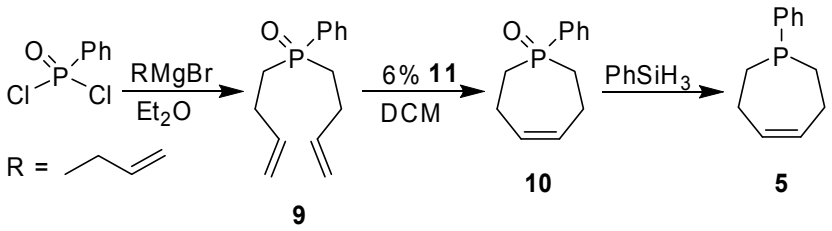
The three systems are discussed separately, starting each section with the synthesis of the 7-membered ring. Of the possible phosphinidene precursors,[5] we use the established 7-phosphanorbornadiene unit **8**.



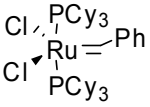
M = W, Mo, Cr

8

Diphos basket 18. The starting point is the synthesis of **5** (Scheme 1). The key step is the ring closing metathesis (RCM) of diene **9**, obtained from reaction of phenylphosphonic dichloride with two equivalents of butenylmagnesium bromide,[6] in the presence of 6% of Grubbs first generation catalyst [$RuCl_2(PCy_3)_2$=CHPh] **11**.[7] Reduction of the resulting oxide **10** at 80 °C with phenylsilane[8] gave the desired tetrahydrophosphepine **5** without side products, as shown by the clean conversion of the ^{31}P resonance at +41.7 to -13.5 ppm.



9 **10** **5**

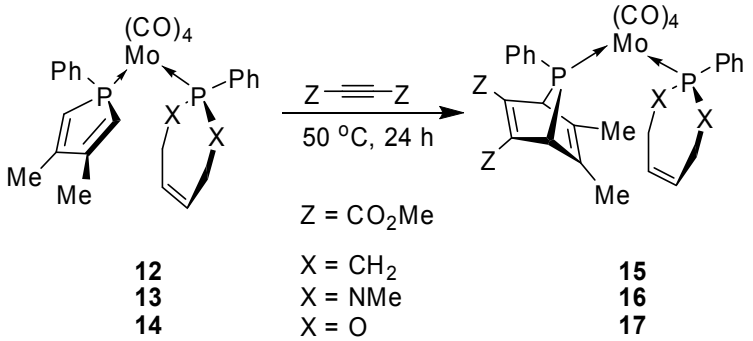


11

Scheme 1. Synthesis of tetrahydrophosphepine **5**

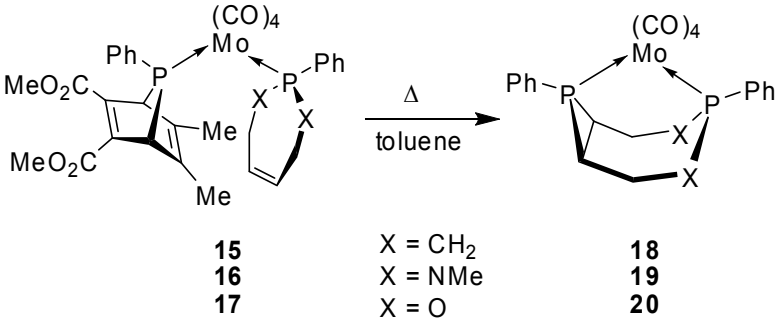
Because **5** is sensitive toward oxidation, it was not isolated but reacted directly with *cis*-$Mo(CO)_4$[piperidine]$_2$[9] and 1-phenyl-3,4-dimethylphosphole. The expected mixed chelated Mo-complex **12** (44%) was formed together with smaller amounts of the bistetrahydrophosphepine (<10%) and bisphosphole Mo-complexes (<10%) as suggested by their resonances at 25.1 and 33.5 ppm in the ^{31}P NMR spectrum. Product **12** shows two doublets at δ = 26.1 and 32.7 ppm with a normal ^2J(P,P) coupling constant of 24.0 Hz. Both the IR carbonyl frequencies at 2021, 1915 and 1890 cm^{-1} and the ^{13}C NMR carbonyl resonances at 215.5, 215.2 and 210.1 ppm confirm that the crucial *cis*-configuration of the transition metal is maintained.

Next, the phosphole ring must be converted to the phosphinidene precursor for the critical cycloaddition to the olefinic bond of the 7-membered ring ligand. Precursor **15** is obtained (63%) in the usual manner by Diels-Alder reaction with dimethyl acetylene dicarboxylate. Again, the complex maintains its *cis*-configuration.



Scheme 2. Synthesis of the 7-phosphanorbornadiene Mo-complexes

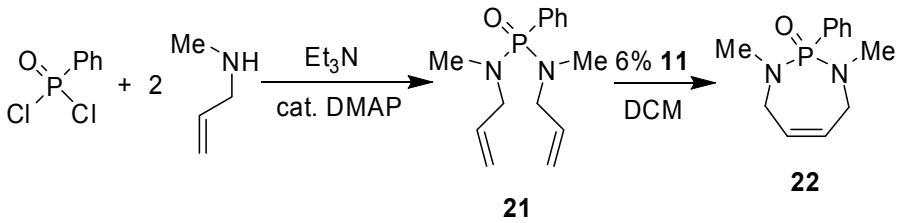
Product **15** shows 2 doublets at δ = 25.7 and 251.9 ppm, of the phosphepine and 7-phosphanorbornadiene P respectively, with a normal ^2J(P,P) coupling constant of 26.1 Hz. The large downfield shift from phosphole to 7-phosphanorbornadiene is normal



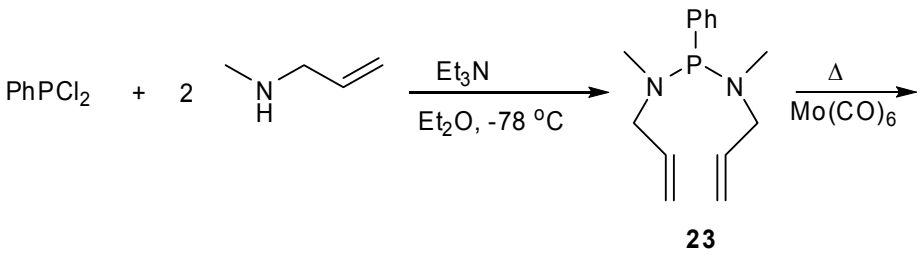
Scheme 3. Phosphinidene addition yielding novel diphos baskets (**18**-**20**)

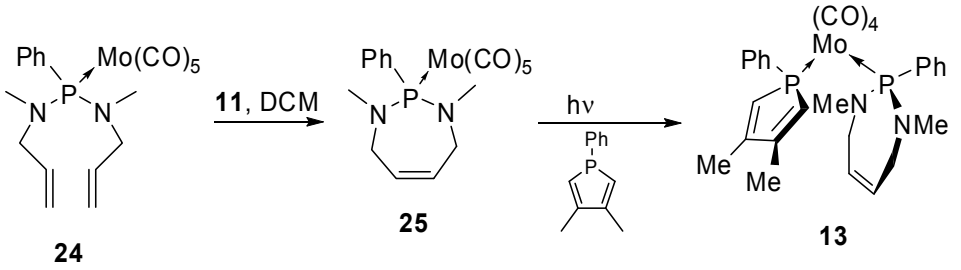
Heating complex **15** in toluene at 80 °C gave, via thermal decomposition of the 7-phosphanorbornadiene ligand to generate the transient phosphinidene complex, indeed the desired cycloadduct **18** as sole isolable, high melting (mp 194-195°C) product (66%) (Scheme 3). The ^{31}P NMR spectrum exhibits two doublets (^2J(P,P) = 38.4 Hz), one at +16.5 ppm for the phosphepane ring and one at -150.5 ppm for the phosphirane

ring. $Mo(CO)_5$-complexed phosphiranes have more deshielded resonances in the -115 to -135 ppm range,[10,11] while those for **1** (-101.7 ppm) and **2** (-79.7 ppm) are at still lower field with no (**1**) or only a small ^2J(P,P) coupling constant (**2**, 8.1 Hz). The $\delta(^{31}P)$ of 15.4 ppm for the phospholane ring of **2** is similar to that of the phosphepane ring of **18**, but also here the ring size effect seems present on comparing the chemical shifts of the 'basket' and its precursor. **18** shows an upfield shift of 9.2 ppm compared to **15** and an *increase* of 12.3 Hz for ^2J(P,P), while ring closure leading to **2** gives a 18.3 Hz *decrease* in ^2J(P,P) and a smaller upfield shift of 4.2 ppm for the 5-membered ring phosphorus. No strain effects are evident from the ^{13}C NMR parameters of the hydrocarbon frame of **18**, neither in comparison with **2**.



Scheme 4. Synthesis of phosphine oxide **22**





Scheme 5. Synthesis of complex **13**

Diphos basket 19. The synthesis of 7-membered ring structure **6** was pursued like that for **5** (Scheme 4), following a procedure described for the related phosphonamides.[12] While, N-methylallylamine (2 equivalents) reacted with $PhP(O)Cl_2$ to give **21** (67%) and whereas ring closing metathesis with Grubbs 1st generation catalyst yielded oxide **22** (78%), no reduction occurred with $PhSiH_3$ or $HSiCl_3/Et_3N$. Therefore, the approach outlined in Scheme 5 was followed. In this route N-methylalylamine is reacted with phenyldichlorophosphine instead of the oxide, giving **23** (95%), so that the stabilizing transition metal group, using freshly prepared $Mo(CO)_5$[MeCN] or $Mo(CO)_6$,[13] is added (**23** → **24** (30%)) before the RCM step (**24** → **25** (97%)). The ^{31}P NMR spectrum shows that the introduction of $Mo(CO)_5$ is frustrated by the formation of unidentified products (138, 146 and 150 ppm) in nearly equal ratio (combined) to main product **24** (126.0 ppm). The *cis*-CO ligand was exchanged for 1-phenyl-3,4-dimethyl-phosphole by UV-irradiation (THF) to give Mo-complex **13** (28%; 51% conversion). Full conversion was not feasible because of the limited stability of **13** under the reaction conditions. Diels-Alder reaction of the phosphole ligand with dimethyl acetylenedicarboxylate yielded phosphinidene precursor complex **16** (55%). Thermal decomposition of this complex at 70 °C in toluene gave diphosphine basket **19** in low yield (24%) as colorless crystals (mp 83-84°C) and minor unidentified products (δ(^{31}P) 135 and 148 ppm). The much lower yield of **19** as compared to **18**

indicates less selectivity for the cycloaddition, possibly due to the competing formation of an ylid that results on interacting the transient phosphinidene complex with the nitrogen atom. Related P,N-ylids are known as reactive intermediates,[14] but are not amenable to isolation and we expect that to be the case here too. The ring closure of **16** to **19** causes an upfield shift of only 2.4 ppm to δ(^{31}P) 140.0 ppm for the 7-membered heterocycle but the 32.1 Hz increase in the ^{2}J(P,P) coupling constant to 58.7 Hz is large. However the NMR spectroscopic data provide little additional insight.

The formation of **19** was ascertained by a single crystal X-ray structure determination (Figure 1). The distorted octahedral conformation around Mo with a small Mo1-C22-O4 bond angle (170.42(16)°) and a larger than usual P2-Mo1-C22 bond angle (99.07(5)°) is due to interaction of the C5-methyl group at N1 with the C22-O4 carbonyl group. The P-Mo-P bite angle of 76.240(13)°) is significantly larger than for the tighter **2** (69.732(16)°) and only 2.6° smaller than for the 5-membered chelate (dppe)Mo(CO)$_4$.[15]. The Mo1-P1 and Mo1-P2 bond lengths of respectively 2.5079(4) and 2.4917(4) Å are in the normal range.[1,16] The steric congestion caused by the methyl group at N1 is also reflected in 7-membered ring with the P1-N1 bond (1.7144(13) Å) being slightly longer than the P1-N2 bond (1.6726(13) Å) and with smaller bond angles around N1 (P1-N1-C1 (114.99(10)°) and P1-N1-C5 (117.16(11)°) *vs* P1-N2-C4 (121.49(10)°) and P1-N2-C6 121.21(11)°). While the nitrogen centers of the molecules in the crystal are chiral, the whole crystal is racemic (centrosymmetric space group). In solution pyramidal inversion of the nitrogen atoms is rapid.

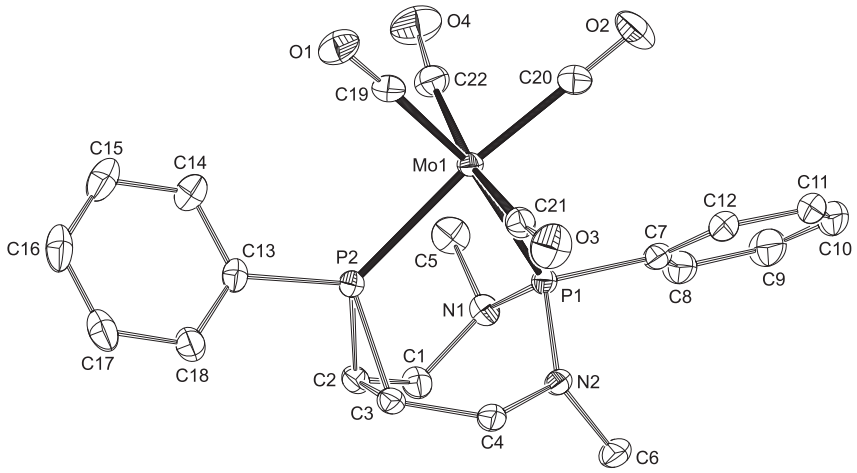


Figure 1 Displacement ellipsoid plot of **19** drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å], angles and torsion angles [°]: Mo1–P1 2.5079(4), Mo1–P2 2.4917(4), P1–N1 1.7144(13), P1–N2 1.6726(13), P2–C2 1.8538(15), P2–C3 1.8317(16), C1–N1 1.474(2), C4–N2 1.4760(19), C5–N1 1.470(2), C6–N2 1.4701(19), C1–C2 1.535(2), C2–C3 1.526(2), C3–C4 1.525(2). P1–Mo1–P2 76.240(13), P1–Mo1–C20 98.26(5), P1–Mo1–C21 92.30(4), P1–Mo1–C22 95.44(5), P2–Mo1–C19 91.82(5), P2–Mo1–C21 92.12(5), P2–Mo1–C22 99.07(5), Mo1–P1–N1 115.26(5), Mo1–P1–N2 114.10(5), Mo1–P1–C7 118.07(5), Mo1–P2–C13 125.31(5), N1–P1–N2 101.81(7), C2–P2–C3 48.90(7), P1–N1–C1 114.99(10), P1–N2–C4 121.49(10), P1–N1–C5 117.16(11), P1–N2–C6 121.21(11), P2–C2–C3 64.79(8), P2–C3–C2 66.30(8), P2–C2–C1 124.47(11), P2–C3–C4 118.81(11), N1–C1–C2 118.48(13), N2–C4–C3 117.41(13), P1–N1–C1–C2 43.94(18), P1–N2–C4–C3 39.03(18), N1–C1–C2–C3 –72.6(2), C2–C3–C4–N2 21.1(2), C1–C2–C3–P2 116.27(14), P2–C2–C3–C4 –110.09(15).

Diphos basket 20. Phosphonite **7** was synthesized in a single step (75%) by condensing *cis*-but-2-ene-1,4-diol with dichlorophenylphosphine using triethylamine as base. Purification by distillation reduces the yield drastically.[17] Synthesis of **7** analogous to **5** is not a viable alternative as the sluggish RCM occurs in poor yield.[12] Reaction of **7** with *cis*-$Mo(CO)_4$[piperidine]$_2$ and 1-phenyl-3,4-dimethylphosphole afforded **14** (30%). The Diels-Alder reaction with dimethyl acetylenedicarboxylate gave **17** (69%). Thermal decomposition at 80 °C in toluene gave the desired very stable diphosphine basket **20** in reasonable isolated yield (61%) as colorless crystals (mp 169-170 °C). Like for **19** ring closure causes essentially no

deshielding (0.9 ppm) of the $\delta(^{31}P)$ for the 7-membered ring (**20** 140.0 ppm), but the $^{2}J(P,P)$ coupling constant (**20** 66.8 Hz) increases more (34.2 Hz). Also in this case do the NMR spectroscopic data provide little additional insight.

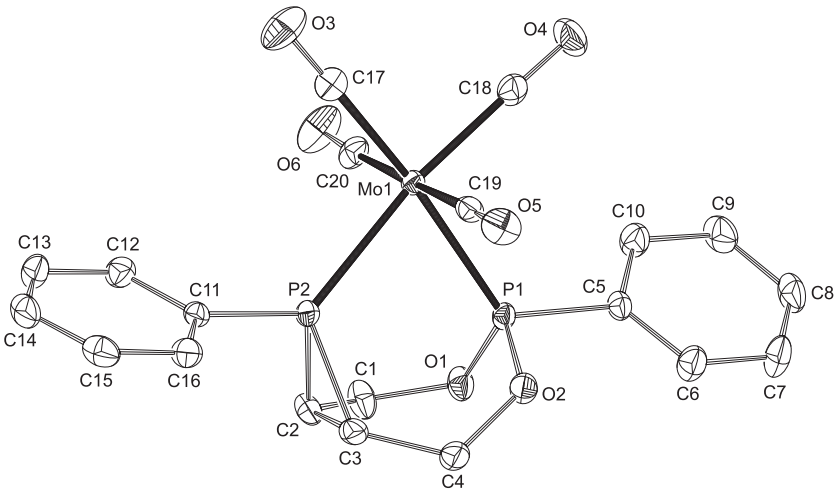


Figure 2 Displacement ellipsoid plot of **20** drawn at the 50% probability level. Selected bond lengths [Å], angles and torsion angles [°]: Mo1-P1 2.4624(4), Mo1-P2 2.4606(4), P1-O1 1.6122(11), P1-O2 1.6229(10), P2-C2 1.8309(15), P2-C3 1.8330(15), C1-O1 1.4457(18), C4-O2 1.4399(18), C1-C2 1.512(2), C2-C3 1.525(2), C3-C4 1.512(2). P1-Mo1-P2 77.626(12), P1-Mo1-C18 94.75(4), P1-Mo1-C19 85.92(4), P1-Mo1-C20 95.76(4), P2-Mo1-C17 96.32(5), P2-Mo1-C19 86.94(4), P2-Mo1-C20 93.38(4), Mo1-P1-O1 119.42(4), Mo1-P1-O2 110.58(4), Mo1-P1-C5 123.14(5), Mo1-P2-C11 129.20(5), O1-P1-O2 101.77(6), C2-P2-C3 49.20(7), P1-O1-C1 122.99(9), P1-O2-C4 119.99(9), P2-C2-C3 65.47(8), P2-C3-C2 65.32(8), P2-C2-C1 119.59(11), P2-C3-C4 125.06(11), O1-C1-C2 115.76(13), O2-C4-C3 118.32(12), P1-O1-C1-C2 -40.05(19), P1-O2-C4-C3 -30.58(19), O1-C1-C2-C3 -18.7(2), C2-C3-C4-O2 61.4(2), C1-C2-C3-P2 110.41(15), P2-C2-C3-C4 -116.67(15).

A single crystal X-ray structure determination of **20** shows the same features as for **19** except that the octahedral conformation around Mo is less distorted, which is reflected in the smaller *cis*-P-Mo-C bond angles. The P1-Mo-P2 bond angle of 77.626(12)°) is similar in magnitude to that of **19**. The two P-Mo distances of **20** (2.4624(4) and 2.4606(4) Å) are virtually of the same length. They are about 0.04 Å shorter than those of **1**, **2**, and

19 and other $Mo(CO)_n$ complexed phosphiranes,[1,16] but similar to those of $RO(R')_2PMo(CO)_5$ (2.436 Å) and $(RO)_3PMo(CO)_5$ (2.485 Å);[18] we are not aware of structural data on phosphonite Mo-complexes, $(OC)_5MoP(OR)_2R'$. The P-O bonds (1.6122(11) and 1.6229(10) Å) are slightly longer than usual.[18]

2.4 Conclusions

The synthesis of the novel Mo-complexes **18-20** expands the access to a new class of unsymmetrical diphos chelates in which the chains (C-C-X vs C-C) connecting the phosphorus atoms and the substitution pattern (X = CH_2, NCH_3, O) around one of them can be varied. They particularly extend to small number of O- and N-containing diphos chelates. The novel 'baskets' were obtained by metal-template-directed *intra*molecular addition of the $Mo(CO)_4L$ phosphinidene complex to the double bond of the 7-membered ring ligand L, i.e., 2,3,6,7-tetrahydro-1*H*-phosphepine **5,** (1,3-dimethyl-2,3,4,7-tetrahydro-1*H*-1,3,2-diazophosphepine) **6**, and 4,7-dihydro-1,3,2-dioxaphosphepine **7**. Complex **18** and the dioxygen containing **20** are very stable on heating contrary to the nitrogen homologue **19**, which may explain its lower yield of formation. The ^{31}P NMR resonances for the phosphirane ring are at similar high field (ca. -150 ppm) for all three complexes, but the already large ^{2}J(P,P) coupling constants increase from 38.1 to 58.7 to 66.8 Hz for **18**, **19**, and **20**, respectively. The crystal structures of **19** and **20** show small P-Mo-P bite angles of 76.240(13)° and 77.626(12)°, respectively. The new compounds are strong chelating complexes as the transition metal group could not be liberated from the ligand by either heating with sulfur,[19] oxidation by iodine followed by ligand exchange,[20] or ligand displacement with bis(diphenylphosphino)ethane.[10]

2.5 Experimental

All experiments were performed under an atmosphere of dry nitrogen. Solids were dried in vacuum and liquids were distilled under N_2 prior to use. Toluene was distilled over sodium and THF was dried by successive distillation over $LiAlH_4$ and sodium/benzophenone. Diethyl ether was distilled over $LiAlH_4$. CH_2Cl_2 was dried over P_2O_5. *Cis*-[bis-(piperidine)]$Mo(CO)_4$[9] and 1-phenyl-3,4-dimethylphosphole[21] were prepared according to literature procedures. NMR spectra were recorded on a Bruker WM 250 spectrometer (^1H, ^{13}C), internally referenced to residual solvent resonances and 85% H_3PO_4 (^{31}P) as external standard. IR spectra were recorded on a Mattson 6030 Galaxy FT-IR spectrophotometer and high-resolution mass spectra (HR-MS) on a Finnigan Mat 900 spectrometer. Melting points were measured on samples in unsealed capillaries and are uncorrected.

Synthesis of *cis*-(3,4-Dimethyl-1-phenyl-1*H*-phosphole)(1-phenyl-2,3,6,7-tetrahydro-1*H*-phosphepine) tetracarbonylmolybdenum (12):

*Synthesis of 1-phenyl-2,3,6,7-tetrahydro-1H-phosphepine 1-oxide **10***:

To a solution of diene **9** (2.5 g, 10.7 mmol) in dichloromethane (0.02 M) was added 6 mol% Grubbs catalyst **11** in 2mol% portions. The reaction was heated at reflux until full conversion of starting material, as shown by ^{31}P NMR. Solvent was then evaporated and product **10** purified by column chromatography (silica gel, ethyl acetate/ethanol 10:1) to yield a colorless solid (955 mg, 44%). A publication by Gouverneur *et al* reports 89% isolated yield [7]. Product characterization was not included in this report. M.p. 75-76 °C; ^{31}P NMR ($CDCl_3$): δ = 41.7 (s); ^1H NMR ($CDCl_3$): δ = 1.85-2.09 (m, 4H; P-CH_2), 2.15-2.40 (m, 2H; CH_2-C=), 2.80-2.91 (m, 2H; CH_2-C=), 7.46-7.51 (m, 3H; Ar), 7.69-7.77 (m, 2H; Ar); ^{13}C NMR: ($CDCl_3$) δ = 19.4 (d, ^2J(C,P) = 5.0 Hz; CH_2), 29.3 (d, ^1J(C,P) = 66.0 Hz; CH_2-P), 128.8 (d, ^2J(C,P) = 11.2 Hz; *o*-Ph), 130.1 (d, ^3J(C,P) = 9.0 Hz; *m*-Ph), 131.8 (d, ^4J(C,P)

= 2.7 Hz; *p*-Ph), 132.4 (s, =CH phosphepine), 134.1 (d, ^{1}J(C,P) = 94.5 Hz; *i*-Ph); HR-MS: calcd. for $C_{12}H_{15}OP$ 206.0861, Found: 206.08671 (δ 2x10^{-3});

*Reduction of **10** to phosphine **5**:*

500 mg (2.43 mmol) 1-phenyl-2,3,6,7-tetrahydro-1H-phosphepine 1-oxide (**10**) was dissolved in 2.4 mL phenylsilane. The mixture was heated for 4 hours at 80 °C. Excess phenylsilane was evaporated under reduced pressure and the resulting oil extracted with hexane (2x10 mL). Product **5** is very sensitive towards oxygen and was used without further purification. ^{31}P NMR (Hexane): δ = -13.5 (s);

*Synthesis of cis-[phosphole][phosphepine]Mo-complex **12**:*

A mixture of *cis*-[bis(piperidine)]Mo(CO)$_4$ (0.925 g, 2.42 mmol) and 1-phenyl-3,4-dimethylphosphole (0.462 g, 2.42 mmol) was stirred in 20 mL refluxing dichloromethane for 10 minutes. 1-Phenyl-2,3,6,7-tetrahydro-1H-phosphepine was added and the mixture was stirred at reflux for an additional 2 hours. Evaporation to dryness and column chromatography (silica gel, pentane/dichloromethane 4:1) afforded **12** (600 mg, 41%) as a yellow solid. Recrystallization from dichloromethane / hexane gave yellow crystals. M.p. 104-105 °C; ^{31}P NMR ($CDCl_3$): δ = 26.1 (d, ^{2}J(P,P) = 24.0 Hz; phosphepine), 32.7 (d, ^{2}J(P,P) = 24.0 Hz; phosphole); ^{1}H NMR ($CDCl_3$): δ = 2.02 (s, 6H, CH_3), 2.14-2.38 (m, 8H; CH_2 & CH_2-P), 5.74 (m, 2H; phosphepine-CH), 6.15 (d, ^{2}J(H,P) = 36.0 Hz; 2H, phosphole-CH), 7.26-7.36 (m; 10H, Ar); ^{13}C NMR: ($CDCl_3$) δ = 17.7 (d, ^{3}J(C,P) = 9.9 Hz; CH_3), 23.4 (d, ^{2}J(C,P) = 4.5 Hz; CH_2), 28.9 (dd, ^{1}J(C,P) = 18.4 Hz, ^{3}J(C,P) = 2.0 Hz; CH_2-P), 128.6-131.3 (m, Ar), 131.1 (dd, ^{1}J(C,P) = 35.4 Hz, ^{3}J(C,P) = 1.8 Hz; P-CH), 131.6 (s; CH_2C=), 133.5 (dd, ^{3}J(C,P) = 1.7 Hz, ^{1}J(C,P) = 16.0 Hz; phosphole *ipso*-Ph), 139.0 (dd, ^{3}J(C,P) = 1.6 Hz, ^{1}J(C,P) = 27.2 Hz; phosphepine *ipso*-Ph), 149.0 (d, ^{2}J(C,P) = 7.8 Hz; CHCCH$_3$), 210.1 (t, ^{2}J(C,P) = 9.2 Hz; CO_{ax}), 215.2 (dd, ^{2}J(C,P) = 8.2 Hz, ^{2}J(C,P) = 16.0 Hz; CO_{eq}), 215.5 (dd, ^{2}J(C,P) = 8.7 Hz, ^{2}J(C,P) = 21.3 Hz; CO_{eq}); HR-MS: calcd. for

$C_{28}H_{28}O_4P_2Mo$ 588.0518, Found: 588.04955 (δ 2x10^{-3}); IR (CH_2Cl_2): ν(CO) = 2017 cm^{-1} (m), 1907 cm^{-1} (s), 1871 cm^{-1} (sh);

Synthesis toward (3,4-Dimethyl-1-phenyl-1H-phosphole)(1,3-dimethyl-2-phenyl-2,3,4,7-tetrahydro-1H-[1,3,2]diazaphosphepine) tetracarbonyl-molybdenum (13):

*Synthesis of phosphine **21***:

A solution containing $PhP(O)Cl_2$ (975 mg, 5.0 mmol), Et_3N (1.01 g, 10 mmol) in 25 mL dichloromethane was slowly added to a stirred solution of methylallylamine (710 mg, 10 mmol) and a catalytic amount of DMAP (31 mg, 0.05 mmol) in 50 mL dichloromethane at 0 °C. After 2 hours, solvent was evaporated and 50 mL diethylether was added to yield a yellow solution and light yellow salts. The solution was filtrated and salts washed with 10 mL diethylether. Evaporation and column chromatography (silica gel, ethyl acetate/MeOH 95:5) yields **21** (890 mg, 67%) as a colorless oil. ^{31}P NMR ($CDCl_3$) δ = 30.0 (s); ^{1}H NMR ($CDCl_3$) δ = 2.58 (d, ^3J(H,P) = 10.0 Hz, 6H; N-CH_3), 3.57 (m, 4H; CH_2-N), 5.10-5.19 (m, 4H; =CH_2), 5.63-5.77 (m, 2H; CH), 7.43-7.47 (m, 3H; Ar), 7.73-7.81 (m, 2H; Ar); ^{13}C NMR ($CDCl_3$) δ = 33.1 (d, ^2J(C,P) = 3.5 Hz; N-CH_3), 51.5 (d, ^2J(C,P) = 4.2 Hz; N-CH_2), 117.6 (s, =CH_2), 128.5 (d, ^2J(C,P) = 13.1 Hz; *o*-Ph), 131.3 (d, ^1J(C,P) = 154.4 Hz; *i*-Ph), 131.5 (d, ^4J(C,P) = 2.8 Hz; *p*-Ph), 132.2 (d, ^3J(C,P) = 8.7 Hz; *m*-Ph), 134.9 (d, ^3J(C,P) = 5.1 Hz; CH=); HR-MS: calcd. for $C_{14}H_{21}N_2OP$ 264.1391, Found: 264.13998 (δ 6x10^{-3});

Synthesis of 1,3-Dimethyl-2-phenyl-1,3,4,7-tetrahydro[1,3,2]diaza-phosphepine 2-oxide (***22***) *by ring closing metathesis of **21***:

Phosphine **21** (500 mg, 1.9 mmol) was dissolved in 100 mL dichloromethane. To this solution was added catalyst **11** (47 mg, 0.06 mmol). The purple solution was heated at reflux for 3 hours. After evaporation of solvent and column chromatography (silica gel, ethyl acetate/methanol 95:5), **22** (350 mg, 78 %) was isolated as a colorless oil.

^{31}P NMR ($CDCl_3$) δ = 32.3 (s); ^{1}H NMR ($CDCl_3$) δ = 2.69 (d, ^{3}J(H,P) = 9.5 Hz, 6H; N- CH_3), 3.44-3.57 (m, 2H; CH_2-N), 3.71-3.85 (m, 2H; CH_2-N), 5.68 (t, ^{3}J(H,H) 2.4 Hz, 2H; =CH_2), 7.44-7.49 (m, 3H; Ar), 7.78-7.85 (m, 2H; Ar); ^{13}C NMR ($CDCl_3$) δ = 36.1 (d, ^{2}J(C,P) = 4.4 Hz; CH_3), 48.0 (d, ^{2}J(C,P) = 2.8 Hz; CH_2), 127.6 (s; CH=), 128.6 (d, ^{2}J(C,P) = 13.3 Hz; *o*-Ph), 130.2 (d, ^{1}J(C,P) = 159.9 Hz; *i*-Ph), 131.7 (d, ^{4}J(C,P) = 2.8 Hz; *p*-Ph), 132.5 (d, ^{3}J(C,P) = 8.8 Hz; *m*-Ph); HR-MS: calcd. for $C_{12}H_{27}N_2OP$ 236.1078, Found: 236.10786 (δ 4x10^{-4});

Synthesis of N,N'-diallyl-N,N'-dimethyl-P-phenyl phosphonous diamide (**23**):

$PhPCl_2$ (0.712 mL, 5.2 mmol) was dissolved in 25 mL of dry diethylether and cooled to -78 °C. A mixture of 1.00 mL (10.5 mmol) allylmethylamine and 1.5 mL (10.5 mmol) triethylamine was slowly added using a dropping funnel. The reaction mixture was slowly warmed up to room temperature after which the salts were filtered off. Evaporation of the solvent yielded 1.23 g (95%) of diaminophosphine **23** of sufficient purity for further use. ^{31}P NMR ($CDCl_3$) δ = 102.3 (s); ^{1}H NMR ($CDCl_3$) δ = 2.61 (d, ^{3}J(H,P) = 6.5 Hz, 6H; N-CH_3), 3.63-3.69 (m, 4H; CH_2-N), 5.13-5.23 (m, 4H; =CH_2), 5.80-5.91 (m, 2H; CH), 7.28-7.45 (m, 5H; Ar);

Synthesis of N,N'-diallyl-N,N'-dimethyl-P-phenyl phosphonous diamide pentacarbonylmolybdenum (**24**):

a) A solution containing $Mo(CO)_5MeCN$ was prepared according to literature procedures[22] from 1.32 gram (5 mmol) $Mo(CO)_6$. A solution containing phosphine **23** (1.27 g, 5.0 mmol] in 10 mL hexane was slowly added. ^{31}P NMR showed the formation of several unidentified products. Column chromatography (silica gel, hexane) afforded 470 mg (0.97 mmol) (20% yield) of complex **24** as a thick oil.

b) A solution containing $Mo(CO)_6$ (4.84 gram, 18.5 mmol) and phosphine **23** (3.67 gram, 14.8 mmol) was heated at 100 °C in methylcylcohexane (100 mL) for 3 hours. ^{31}P NMR showed the formation of several products, most of them being identical to those obtained by method a. After cooling to room temperature, the excess of $Mo(CO)_6$ was filtered off. The remaining yellow solution was evaporated under reduced pressure. Column chromatography (silica gel, pentane) afforded 2.15 gram (30%) of the complexed phosphine **24** as a thick oil which solidified in the freezer. M.p. 31–32 °C; ^{31}P NMR ($CDCl_3$) δ = 126.0 (s); ^{1}H NMR ($CDCl_3$) δ = 2.72 (d, ^{3}J(H,P) = 10.0 Hz, 6H; CH_3), 3.70–3.91 (m, 4H; CH_2–N), 5.23–5.31 (m, 4H; =CH_2), 5.73–5.86 (m, 2H; CH), 7.26–7.60 (m, 5H; Ar); ^{13}C NMR ($CDCl_3$) δ = 37.7 (d, ^{2}J(C,P) = 1.8Hz; CH_3), 56.7 (d, ^{2}J(C,P) = 8.5Hz; CH_2–N), 118.2 (s; =CH_2), 129.2–130.8 (m, Ar), 135.8 (d, ^{3}J(C,P) = 6.5 Hz; CH), 141.7 (d, ^{1}J(C,P) = 61.7 Hz; phosphepine *ipso*–Ph), 205.7 (d, ^{2}J(C,P) = 9.8 Hz; CO_{ax}), 211.4 (d, ^{2}J(C,P) = 27.6 Hz; CO_{eq}); HR–MS: calcd. for $C_{19}H_{21}N_2O_5PMo$ 486.0242, Found: 486.02322 (δ 1x10^{-3}); IR(CH_2Cl_2): ν(CO) = 2071 cm^{-1} (m), 1943 cm^{-1} (s);

Synthesis of 1,3–Dimethyl–2–phenyl–1,3,4,7–tetrahydro–[1,3,2]diazaphos–phepine pentacarbonylmolybdenum (***25***) *by ring closing metathesis of* ***24***:
Complex **24** (470 mg, 0.97 mmol) was dissolved in 25 mL dichloromethane. 2 mol% of RCM–catalyst **11** (16 mg, 0.02 mmol) was added and the mixture was heated at reflux temperature for 10 minutes. After evaporation of the solvent and column chromatography (silica gel, *n*–hexane), complex **25** (430 mg, 97%) was isolated as a white solid. M.p. 136–137 °C (decomp.); ^{31}P NMR ($CDCl_3$) δ = 135.1 (s); ^{1}H NMR ($CDCl_3$) δ = 3.07 (d, ^{3}J(H,P) = 14.5 Hz, 6H; CH_3), 3.13–3.27 (m, 2H; CH_2–N), 4.26–4.35 (m, 2H; CH_2–N), 6.10–6.15 (m, 2H; CH), 7.36–7.68 (m, 5H; Ar); ^{13}C NMR ($CDCl_3$) δ = 41.1 (d, ^{2}J(C,P) = 14.34 Hz; CH_3), 48.8 (d, ^{2}J(C,P) = 7.2 Hz; CH_2–N), 129.5–130.6 (m, Ar), 135.1 (s, CH), 141.8 (d, ^{1}J(C,P) = 63.7 Hz; *ipso*–Ph), 205.8 (d, ^{2}J(C,P) = 9.9 Hz; CO_{ax}), 211.5 (d, ^{2}J(C,P) = 27.1 Hz;

CO_{eq}); HR-MS: calcd. for $C_{17}H_{27}N_2O_5PMo$ 457.9929, Found: 457.99393 (δ 1x10^{-3}); IR(CH_2Cl_2): ν(CO) = 2072 cm^{-1} (w), 1944 cm^{-1} (s);

*Synthesis of **13** by irradiation of **25** in the presence of phenylphosphole):* A solution of complex **25** (1.55 g, 3.4 mmol) and 1-phenyl-3,4-dimethylphosphole (637 mg, 3.4 mmol) in 100 mL THF was prepared. This mixture was irradiated for 5 hours employing a high pressure Philips Hg lamp (0.9 A, Type 93110E), while N_2-gas was bubbled through the solution at a slow rate. Evaporation of THF and subsequent column chromatography starting with pentane and gradually changing to pentane/dichloromethane 4:1 resulted in the isolation of complex **13** (580 mg, 28%) as a yellow solid. Furthermore, compound **25** (700 mg, 45%) was recovered and could be re-used. Yields are calculated compared to 3.4 mmol starting material used and not corrected for recovery of **25**. Recrystallization of **13** in DCM/hexane gave yellow crystals. M.p. 142-143 °C; ^{31}P NMR ($CDCl_3$) δ = 32.3 (d, ^2J(P,P) = 25.5 Hz; phosphole), 138.2 (d, ^2J(P,P) = 25.5 Hz; phosphepine); ^{1}H NMR ($CDCl_3$) δ = 2.07 (s, 6H; phosphole-CH_3), 2.92 (d, ^3J(H,P) = 14.1 Hz, 6H; N-CH_3), 3.11-3.25 (m, 2H; CH_2-N), 4.14-4.23 (m, 2H; CH_2-N), 6.00 (m, 2H; phosphepine HC=), 6.40 (d, ^2J(H,P) = 35.3 Hz, 2H; phosphole HC=), 7.26-7.60 (m, 10H; Ar); ^{13}C NMR ($CDCl_3$) δ = 17.6 (d, ^3J(C,P) = 10.1 Hz; phosphole-CH_3), 40.0 (dd, ^4J(C,P) = 2.0 Hz, ^2J(C,P) = 15.0 Hz; N-CH_3), 49.0 (d, ^2J(C,P) = 6.8 Hz; CH_2-N), 128.7-131.6 (m, Ar), 131.3 (dd, ^3J(C,P) = 11.6 Hz, ^1J(C,P) = 46.7 Hz; phosphole-CH), 133.4 (d, ^1J(C,P) = 32.2 Hz; phosphole *ipso*-Ph), 134.6 (s; phosphepine-CH), 141.7 (d, ^1J(C,P) = 55.7 Hz; phosphepine *ipso*-Ph), 148.7 (d, ^2J(C,P) = 8.11 Hz; P-CH=*C*), 209.3 (dd, ^2J(C,P) = 8.5 Hz, ^2J(C,P) = 10.3 Hz; CO_{ax}), 215.0 (dd, ^2J(C,P) = 9.8 Hz, ^2J(C,P) = 21.1 Hz; CO_{eq}), 216.2 (dd, ^2J(C,P) = 8.6 Hz, ^2J(C,P) = 30.4 Hz; CO_{eq}); HR-MS: calcd for $C_{28}H_{30}N_2O_4P_2Mo$ 618.0735, Found: 618.07009 (δ 2x10^{-3}); IR(CH_2Cl_2): ν(CO) = 2022 cm^{-1} (m), 1908 cm^{-1} (s), 1875 cm^{-1} (sh);

Synthesis of (3,4-Dimethyl-1-phenyl-1H-phosphole)(2-phenyl-4,7-dihydro-[1,3,2]dioxaphosphepine) tetracarbonylmolybdenum (14):

Synthesis of 2-phenyl-4,7-dihydro-1,3,2-dioxaphosphepine **7**:

$PhPCl_2$ (3.58 g, 20.0 mmol) in 50 mL diethylether was slowly added to a solution of triethylamine (4.55 g, 40.0 mmol) and *cis*-but-2-ene-1,4-diol (1.84 g, 20.0 mmol) in 150 mL diethylether at 0 °C and stirred for 1 hour before warming up to room temperature. ^{31}P NMR showed an excellent conversion to the desired product. After filtration of the salts and evaporation of solvent, 3.00 g of **7** (>90% pure by ^{31}P NMR) as a colorless oil was obtained, which could be used without further purification. A minor side product (<10% by ^{31}P NMR) at 21.6 ppm was observed. During distillation, a gummy material was formed reducing the yield dramatically. After distillation at 80 °C/2x10^{-4} mbar, 830 mg (24%) of **7** as an air-sensitive colorless oil was obtained. ^{31}P NMR ($CDCl_3$): δ = 161.1 (s); ^{1}H NMR ($CDCl_3$): δ = 4.45-4.66 (m, 4H; CH_2), 5.75 (t, ^{2}J(H,H) = 1.9 Hz, 2H; CH_2-C*H*), 7.44-7.48 (m; 3H; Ar), 7.68-7.74 (m; 2H; Ar); ^{13}C NMR: ($CDCl_3$) δ 64.0 (s, CH_2), 128.2 (d, ^{4}J(C,P) = 4.9 Hz; *m*-Ph), 129.6 (d, ^{3}J(C,P) = 20.6 Hz; *o*-Ph), 130.0 (s, phosphepine HC=), 131.3 (s, *p*-Ph), 140.8 (d, ^{1}J(C,P) = 32.0 Hz; *i*-Ph);

Synthesis of cis-[phosphole][phosphepine]Mo-complex **14***:*

A mixture of *cis*-[bis(piperidine)]$Mo(CO)_4$ (2.1 g, 5.6 mmol) and 2-phenyl-4,7-dihydro-1,3,2-dioxaphosphepine (**7**) (1.1 g, 5.6 mmol) was stirred in 20 mL refluxing dichloromethane for 10 minutes. 1-Phenyl-3,4-dimethylphosphole (1.0 g, 5.6 mmol) in 10 mL dichloromethane was added and the mixture was stirred at reflux for an additional 3 hours. Evaporation to dryness and column chromatography (silica gel, pentane/dichloromethane 4:1) gave 0.841 g (30 %) of complex **14** as a yellow solid. Recrystallization from diethylether/hexane afforded yellow crystals. M.p. 111-112 °C; ^{31}P NMR ($CDCl_3$): δ = 33.0 (d, ^{2}J(P,P) = 29.0 Hz; phosphole-P), 190.9 (d, ^{2}J(P,P) = 29.0 Hz; O-P); ^{1}H NMR ($CDCl_3$): δ = 2.05

(s, 6H, CH_3), 4.41-4.62 (m, 4H; CH_2), 5.70 (s, 2H; CH, phosphepine), 6.41 (d, ^2J(H,P) = 36.3 Hz, 2H; CH phosphole), 7.29-7.54 (m; 10H; Ar); ^{13}C NMR: ($CDCl_3$) δ = 17.7 (d, ^3J(C,P) = 10.3 Hz; CH_3), 64.6 (d, ^2J(C,P) = 6.0 Hz; CH_2), 128.5-131.5 (m; Ph), 129.4 (s; phosphepine HC=), 131.2 (d, ^1J(C,P) = 35.0 Hz; phosphole HC=), 133.8 (d, ^1J(C,P) = 33.0 Hz; phosphole *ipso*-Ph), 141.2 (d, ^1J(C,P) = 33.8 Hz; phosphepine *ipso*-Ph), 148.9 (d, ^2J(C,P) = 8.2 Hz; CH*C*CH_3), 209.0 (dd, ^2J(C,P) = 8.8 Hz, ^2J(C,P) = 12.1 Hz; *C*O_{ax}), 213.7 (dd, ^2J(C,P) = 11.5 Hz, ^2J(C,P) = 19.4 Hz; *C*O_{eq}), 214.0 (dd, ^2J(C,P) = 8.2 Hz, ^2J(C,P) = 36.6 Hz; *C*O_{eq}); HR-MS: calcd. for $C_{26}H_{24}O_6P_2Mo$ 592.0103, Found: 592.00659 (δ 1x10^{-3}); IR (CH_2Cl_2): ν(CO) = 2025 cm^{-1} (m), 1913 cm^{-1} (s);

Synthesis of *cis*-(5,6-Dimethyl-7-phenyl-7-phospha-bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic acid dimethyl ester)(1-phenyl-2,3,6,7-tetrahydro-1H-phosphepine) tetracarbonylmolybdenum (15): A mixture of complex **12** (0.500 g, 0.85 mmol) and dimethylacetylene dicarboxylate (2.5 mL, 20 mmol) was stirred at 50 °C for 22 hours. Column chromatography over silica gel, starting with pentane as eluent and gradually converting to dichloromethane, gave first recovered dimethylacetylene dicarboxylate, followed by compound **15** (390 mg, 63%) as a yellow oil. Crystallization from dichloromethane/hexane gave yellow crystals. M.p. 131-132 °C; ^{31}P NMR ($CDCl_3$) δ = 25.7 (d, ^2J(P,P) = 26.1 Hz; phosphepine), 251.9 (d, ^2J(P,P) = 26.1 Hz; phosphanorbornadiene-P); ^{1}H NMR ($CDCl_3$) δ = 1.88 (d, ^4J(H,P) = 0.9 Hz, 6H; CH_3), 2.19-2.35 (m, 8H; CH_2-P & CH_2), 3.39 (d, ^2J(H,P) = 2.9 Hz, 2H; phosphanorbornadiene-CH), 3.61 (s, 6H; OCH_3), 5.73 (m, 2H; =CH), 7.26-7.49 (m, 10H; Ar); ^{13}C NMR ($CDCl_3$) δ = 16.2 (d, ^3J(C,P) = 1.8 Hz; CH_3), 23.3 (d, ^2J(C,P) = 5.2 Hz; *C*H_2-C=), 29.2 (dd, ^3J(C,P) = 1.8 Hz, ^1J(C,P) = 19.9 Hz; *C*H_2-P), 52.4 (s, OCH_3), 60.0 (dd, ^3J(C,P) = 2.0 Hz, ^1J(C,P) = 14.3 Hz; phosphonorbornadiene-CH), 128.1-130.4 (m; Ar), 131.7 (s; =CH), 137.7 (d, ^1J(C,P) = 17.4 Hz; phosphanorbornadiene *ipso*-Ph), 139.3 (dd, ^3J(C,P) = 2.4 Hz, ^1J(C,P) = 27.4 Hz; phosphepine *ipso*-Ph), 142.3 (d, ^2J(C,P) = 3.0 Hz; CH*C*CH_3), 146.2 (d, ^2J(C,P) = 3.5 Hz; *C*CO_2CH_3), 165.6 (d,

^3J(C,P) = 2.3 Hz; *C*O_2CH_3), 209.3 (dd, ^2J(C,P) = 8.0 Hz, ^2J(C,P) = 9.8 Hz; CO_{ax}), 214.8 (dd, ^2J(C,P) = 8.8 Hz, ^2J(C,P) = 12.4 Hz; CO_{eq}), 215.3 (dd, ^2J(C,P) = 5.7 Hz, ^2J(C,P) = 8.8 Hz; CO_{eq}); IR (CH_2Cl_2): ν(CO) = 2021 cm^{-1} (m), 1915 cm^{-1} (s), 1890 cm^{-1} (sh); Compound **15** was too unstable for HR-MS. Formation of **18** was observed.

Synthesis of *cis*- (5,6-Dimethyl-7-phenyl-7-phospha-bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic acid dimethyl ester)(1,3-dimethyl-2-phenyl-2,3,4,7-tetrahydro-1H-[1,3,2]diazaphosphepine) tetracarbonylmolybdenum (16): A solution of complex **13** (500 mg, 0.81 mmol) in 1 mL of dichloromethane and 3 mL (24 mmol) of dimethylacetylene dicarboxylate was heated for 28 hours at 45 °C. Column chromatography starting with hexane and gradually changing to dichloromethane as eluent afforded 330 mg (55%) of complex **16** as an orange solid. Recrystallization (DCM/hexane) resulted in the formation of orange needles. M.p. 71-72 °C; ^{31}P NMR ($CDCl_3$) δ = 250.5 (d, ^2J(P,P) = 26.6 Hz; 7-phosphanorbornadiene), 137.6 (d, ^2J(P,P) = 26.6 Hz; phosphepine); ^{1}H NMR ($CDCl_3$) δ = 1.96 (d, ^4J(H,P) = 1.0 Hz, 6H; CH_3), 2.96 (d, ^3J(H,P) = 14.1 Hz, 6H; N-CH_3), 3.13-3.20 (m, 2H; CH_2-N), 3.59 (s, 2H; phosphanorbornadiene-CH), 3.61 (s, 6H; OCH_3), 4.16-4.20 (m, 2H; CH_2-N), 6.00 (m, 2H; phosphepine-CH), 7.04-7.49 (m, 10H; Ar); ^{13}C NMR ($CDCl_3$) δ = 16.2 (d, ^3J(C,P) = 2.1Hz; CH_3), 40.0 (d, ^2J(C,P) = 14.1 Hz; N-CH_3), 49.0 (d, ^2J(C,P) = 6.9 Hz; CH_2-N), 52.3 (s, OCH_3), 60.5 (dd, ^3J(C,P) = 1.4 Hz, ^1J(C,P) = 14.2 Hz; phosphonorbornadiene-CH), 127.9-131.2 (m; Ar), 134.7 (s; =CH), 138.1 (d, ^1J(C,P) = 17.4 Hz; phosphanorbornadiene *ipso*-Ph), 141.7 (dd, ^3J(C,P) = 1.5 Hz, ^1J(C,P) = 57.0 Hz; phosphepine *ipso*-Ph), 141.9 (d, ^2J(C,P) = 2.8 Hz; CH*C*CH_3), 146.7 (d, ^2J(C,P) = 3.6 Hz; *C*CO_2CH_3), 165.7 (d, ^3J(C,P) = 2.1 Hz; *C*O_2CH_3), 208.9 (dd, ^2J(C,P) = 8.2 Hz, ^2J(C,P) = 10.5 Hz; CO_{ax}), 215.0 (dd, ^2J(C,P) = 10.8 Hz, ^2J(C,P) = 28.9 Hz; CO_{eq}), 215.8 (dd, ^2J(C,P) = 10.0 Hz, ^2J(C,P) = 28.2 Hz; CO_{eq}); IR (CH_2Cl_2): ν(CO) = 2024 cm^{-1} (m), 1918 cm^{-1} (s),

1889 cm^{-1} (sh); Compound **16** was too unstable for HR-MS. Formation of compound **19** was observed.

Synthesis of *cis*-(5,6-Dimethyl-7-phenyl-7-phospha-bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic acid dimethyl ester)(2-phenyl-4,7-dihydro-[1,3,2]dioxaphosphepine) tetracarbonylmolybdenum (17): A mixture of complex **14** (0.72 g, 1.2 mmol) and dimethylacetylene dicarboxylate (2.5 mL, 20 mmol) was stirred at 45 °C for 22 hours. Column chromatography over silica gel, starting with pentane as eluent and gradually converting to dichloromethane, gave first recovered dimethylacetylene dicarboxylate, followed by 0.61 g (69%) of complex **17** as a yellow oil. Crystallization from dichloromethane/hexane gives yellow crystals. M.p. 139-140 °C; ^{31}P NMR ($CDCl_3$) δ = 190.8 (d, ^2J(P,P) = 32.6 Hz; phosphepine), 248.8 (d, ^2J(P,P) = 32.6 Hz; phosphanorbornadiene); ^{1}H NMR ($CDCl_3$) δ = 1.97 (d, ^4J(H,P) = 0.8 Hz, 6H; CH_3), 3.63 (s, 6H; OCH_3), 3.77 (d, ^2J(H,P) = 2.6 Hz, 2H; phosphanorbornadiene-CH), 4.45-4.56 (m, 4H; CH_2), 5.75 (s, 2H; =CH), 7.09-7.59 (m, 10H; Ar); ^{13}C NMR ($CDCl_3$) δ = 16.3 (d, ^3J(C,P) = 1.8 Hz; CH_3), 52.4 (s, OCH_3), 60.4 (dd, ^3J(C,P) = 2.0 Hz, ^1J(C,P) = 15.4 Hz; phosphonorbornadiene-CH), 64.8 (d, ^2J(C,P) = 6.1 Hz; OCH_2), 128.1-129.5 (m; Ar), 131.0 (s; =*C*H), 138.0 (d, ^1J(C,P) = 17.4 Hz; phosphanorbornadiene *ipso*-Ph), 141.3 (d, ^1J(C,P) = 34.9 Hz; phosphepine *ipso*-Ph), 142.4 (d, ^2J(C,P) = 4.6 Hz; CH*C*CH_3), 146.4 (d, ^2J(C,P) = 3.7 Hz; *C*CO_2CH_3), 165.7 (d, ^3J(C,P) = 2.3 Hz; *C*O_2CH_3), 208.4 (dd, ^2J(C,P) = 8.3 Hz, ^2J(C,P) = 12.1 Hz; CO_{ax}), 213.2 (dd, ^2J(C,P) = 11.2 Hz, ^2J(C,P) = 26.7 Hz; CO_{eq}), 213.9 (dd, ^2J(C,P) = 9.9 Hz, ^2J(C,P) = 33.7 Hz; CO_{eq}); HR-MS: calcd. for $C_{32}H_{30}O_{10}P_2Mo$ 734.0369, Found: 734.03273 (δ 2x10^{-2}); IR (CH_2Cl_2): ν(CO) 2029 cm^{-1} (w), 1923 cm^{-1} (s);

Synthesis of 4,8-Diphenyl-4,8-diphospha-bicyclo[5.1.0]octane tetra-carbonylmolybdenum (18) by thermal decomposition of 15: A solution of **15** (0.35 g, 0.48 mmol) in 5 mL toluene was stirred at 80 °C for 3 hours.

Evaporation to dryness, column chromatography (silica gel, dichloromethane/pentane 2:1) and recrystallization from dichloromethane/hexane gave **18** (0.160 g, 66%) as colorless crystals. M.p: 194–195°C (decomp); ^{31}P NMR: ($CDCl_3$): δ = –150.5 (d, ^2J(P,P) = 38.4 Hz; phosphirane), 16.46 (d, ^2J(P,P) = 38.4 Hz; phosphepane); ^{1}H NMR: ($CDCl_3$): δ = 2.07–2.38 (m, 6H; CH & CH_2–P), 2.43–2.72 (m, 2H; CH–CH_2), 2.78–2.98 (m, 2H; CH–CH_2) , 7.37–7.60 (m; 10H, Ar); ^{13}C NMR: ($CDCl_3$): δ = 21.9 (d, ^2J(C,P) = 3.4 Hz; CH–*C*H_2), 26.7 (dd, ^1J(C,P) = 20.5 Hz, ^3J(C,P) = 4.0 Hz; CH_2–P), 26.8 (dd, ^3J(C,P) = 4.8 Hz, ^1J(C,P) = 15.4 Hz; CH–P), 128.9–131.4 (m, Ar), 135.8 (dd, ^3J(C,P) = 4.2 Hz, ^1J(C,P) = 11.8 Hz; phosphirane *ipso*–Ph), 138.5 (dd, ^3J(C,P) = 8.4 Hz, ^1J(C,P) = 30.2 Hz; phosphepane *ipso*–Ph), 209.7 (dd, ^2J(C,P) = 9.5 Hz, ^2J(C,P) = 11.4 Hz; CO_{ax}), 214.6 (dd, ^2J(C,P) = 9.2 Hz, ^2J(C,P) = 31.3 Hz; CO_{eq}), 216.4 (dd, ^2J(C,P) = 10.0 Hz, ^2J(C,P) = 22.3 Hz; CO_{eq}); HR–MS: calcd. for $C_{22}H_{20}O_4P_2Mo$ 507.9892, Found: 507.98926 (δ 2x10^{-3}); IR(CH_2Cl_2): ν(CO) = 2019 cm^{-1} (m), 1901 cm^{-1} (s), 1884 cm^{-1} (sh); EI–MS *m/z* (%): 508 (18) [M$^+$], 480 (2) [M$^+$–CO], 452 (24) [M$^+$–2CO], 424 (15) [M$^+$–3CO], 396 (100) [M$^+$–4CO].

Synthesis of 3,5-Dimethyl-4,8-diphenyl-3,5-diaza-4,8-diphospha-bicyclo[5.1.0]octane tetracarbonylmolybdenum (19) by thermal decomposition of 16: A solution of **16** (146 mg, 0.19 mmol) in 3 mL toluene was stirred at 70 °C for 5 hours. Evaporation to dryness, chromatography (silica gel, dichloromethane/pentane 2:1) and recrystallization from dichloro-methane/hexane gave 25 mg (24%) of complex **19** as colorless crystals. A second fraction contained 46 mg (32%) of starting material **16**. M.p. 83–84; °C ^{31}P NMR ($CDCl_3$) δ = –149.1 (d, ^2J(P,P) = 58.7 Hz; phosphirane), 140.4 (d, ^2J(P,P) = 58.7 Hz; phosphepane); ^{1}H NMR ($CDCl_3$) δ = 2.32 (m, 2H; CH), 2.42 (d, ^3J(H,P) = 8.8 Hz, 6H; N–CH_3), 3.60–3.80 (m, 2H; CH_2–N), 4.02–4.11 (m, 2H; CH_2–N), 7.40–7.69 (m, 10H, Ar); ^{13}C NMR ($CDCl_3$) δ = 25.8 (dd, ^1J(C,P) = 14.0 Hz, ^3J(C,P) = 4.8 Hz;

CH), 40.7 (d, ^{2}J(C,P) = 2.5 Hz; N-CH_3), 51.0 (dd, ^{2}J(C,P) = 7.4 Hz, ^{2}J(C,P) = 2.5 Hz; CH_2-N), 128.1-131.2 (m; Ar), 133.8 (dd, ^{3}J(C,P) = 7.7 Hz, ^{1}J(C,P) = 9.6 Hz; phosphirane *ipso*-Ph), 136.3 (dd, ^{3}J(C,P) = 5.8 Hz, ^{1}J(C,P) = 43.7 Hz; phosphepane *ipso*-Ph), 210.5 (dd, ^{2}J(C,P) = 10.1 Hz, ^{2}J(C,P) = 11.4 Hz; CO_{ax}), 214.0 (dd, ^{2}J(C,P) = 10.1 Hz, ^{2}J(C,P) = 31.7 Hz; CO_{eq}), 216.2 (dd, ^{2}J(C,P) = 10.3 Hz, ^{2}J(C,P) = 26.4 Hz; CO_{eq}); HR-MS: calcd for $C_{22}H_{22}N_2O_4P_2Mo$ 538.0109, Found: 538.00991 (δ 6x10^{-3}); IR (CH_2Cl_2): ν(CO) = 2017 cm^{-1} (m), 1900 cm^{-1} (s); EI-MS *m/z* (%): 538 (10) [M^+], 510 (8) [M^+-CO], 482 (10) [M^+-2CO], 454 (10) [M^+-3CO], 426 (45) [M^+-4CO], 374 (45) [M^+-2CO,PPh], 318 (45) [M^+-phosphepine].

Synthesis of 4,8-Diphenyl-3,5-dioxa-4,8-diphospha-bicyclo[5.1.0]octane tetracarbonylmolybdenum (20) by thermal decomposition of 17: A solution of **17** (0.35 g, 0.47 mmol) in 3 mL toluene was stirred at 80 °C for 3 hours. Evaporation to dryness and column chromatography (silica gel, dichloromethane/pentane 2:1) followed by recrystallization from dichloromethane/hexane yielded **20** (0.15 g, 61%) as colorless crystals. M.p. 169-170 °C (decomp); ^{31}P NMR ($CDCl_3$) δ = -150.6 (d, ^{2}J(P,P) = 66.8 Hz; phosphirane), 191.7 (d, ^{2}J(P,P) = 66.8 Hz; phosphepane); ^{1}H NMR ($CDCl_3$) δ = 2.62 (d, ^{2}J(H,P) = 5.6 Hz, 2H; phosphirane-CH), 4.75-5.30 (m, 4H; CH_2), 7.44-7.78 (m, 10H; Ar); ^{13}C NMR ($CDCl_3$) δ = 28.6 (dd, ^{1}J(C,P) = 11.7 Hz, ^{3}J(C,P) = 7.6 Hz; CH), 65.0 (dd, ^{2}J(C,P) = 2.0 Hz, ^{2}J(C,P) = 2.9 Hz; CH_2), 128.6-132.0 (m; Ar), 132.9 (dd, ^{1}J(C,P) = 10.2 Hz, ^{3}J(C,P) = 6.7 Hz;phosphirane *ipso*-Ph), 140.1 (dd, ^{1}J(C,P) = 51.6 Hz, ^{3}J(C,P) = 4.9 Hz; phosphepane *ipso*-Ph), 207.8 (m; CO_{ax}), 212.9 (dd, ^{2}J(C,P) = 10.2 Hz, ^{2}J(C,P) = 29.8 Hz; CO_{eq}), 215.5 (dd, ^{2}J(C,P) = 10.6 Hz, ^{2}J(C,P) = 32.7 Hz; CO_{eq}); HR-MS: calcd. for $C_{20}H_{16}O_6P_2Mo$ 511.9477, Found: 511.94668 (δ 2x10^{-3}); IR (CH_2Cl_2): ν(CO) = 2031 cm^{-1} (w), 1919 cm^{-1} (s); EI-MS *m/z* (%): 512 (40) [M^+], 484 (4) [M^+-CO], 456 (16) [M^+-2CO], 428 (28) [M^+-3CO], 400 (100) [M^+-4CO].

X-ray crystal structure determinations

X-ray intensities were measured on a Nonius Kappa CCD diffractometer with rotating anode and graphite monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1}. The structures were solved with automated Patterson methods[23] and refined with SHELXL-97[24] on F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map. Methyl and phenyl H atoms were refined with a riding model; all other H atoms were refined freely with isotropic displacement parameters. Geometry calculations, drawings and checking for higher symmetry were performed with the PLATON package.[25]

Crystal structure determination of **19**. $C_{22}H_{22}MoN_2O_4P_2$, Fw = 536.30, colourless block, 0.42 x 0.36 x 0.18 mm^3, orthorhombic, Pbca (no. 61), a = 16.48859(15), b = 15.3260(9), c = 18.2133(4) Å, V = 4602.6(3) Å^3, Z = 8, D_x = 1.548 g/cm^3. 110857 Reflections were measured. An absorption correction based on multiple measured reflections was applied (μ = 0.74 mm^{-1}, 0.72-0.88 correction range). 5283 reflections were unique (R_{int} = 0.029). 306 parameters were refined with no restraints. R1/wR2 [$I > 2\sigma(I)$]: 0.0200/0.0457. R1/wR2 [all refl.]: 0.0287/0.0504. S = 1.092. Residual electron density between -0.29 and 0.47 e/Å^3.

Crystal structure determination of **20**. $C_{20}H_{16}MoO_6P_2$, Fw = 510.21, colourless block, 0.45 x 0.42 x 0.36 mm^3, triclinic, $P\bar{1}$ (no. 2), a = 7.5410(1), b = 9.6907(1), c = 14.8771(2) Å, α = 96.2156(11), β = 101.7812(10), γ = 106.0581(10)°, V = 1006.95(2) Å^3, Z = 2, D_x = 1.683 g/cm^3. 16625 Reflections were measured. An absorption correction based on multiple measured reflections was applied (μ = 0.85 mm^{-1}, 0.67-0.74 correction range). 4598 reflections were unique (R_{int} = 0.016). 286 parameters were refined with no restraints. R1/wR2 [$I > 2\sigma(I)$]:

0.0175/0.0416. R1/wR2 [all refl.]: 0.0218/0.0428. S = 1.065. Residual electron density between -0.27 and 0.36 e/Å^3.

CCDC-291538 (compound **19**), and -291539 (**20**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

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Chapter 3

Decomplexation of Phosphirane and Phosphirene Complexes

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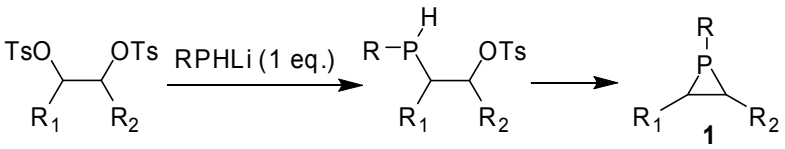
3.1 Abstract

Novel transient phosphinidene complex Ph-P=$Mo(CO)_4PMe_3$, generated from a 7-phosphanorbornadiene precursor, adds to C=C and C≡C bonds to give $Mo(CO)_4PMe_3$ complexed phosphiranes and phosphirenes. The *cis*-PMe_3 ligand weakens the interaction between the molybdenum complex and the three-membered ring. Under mild CO pressure $Mo(CO)_4PMe_3$ transition metal group detaches from the phosphorus center of the ring structure by selective CO substitution. The resulting byproduct $Mo(CO)_5PMe_3$ can be reused in the synthesis of the phosphinidene precursor.

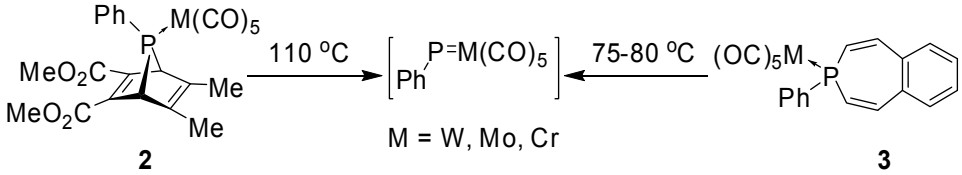
3.2 Introduction

Phosphirane (**1**), the phosphorus homologue of cyclopropane, has received much attention in the past two decades as new synthetic routes became available that make use of the stabilization rendered by transition metal groups.[1] Whereas uncomplexed phosphiranes can be obtained, for example, from the reaction of a metal phosphide and a diol ditosylate (see Scheme 1),[2] their limited thermal stability and sensitivity toward oxidation not only complicates their isolation but also restricts the versatility of the reaction. Phosphiranes have also been synthesized by carbene addition to a phosphaalkene, by salt elimination from the reaction of RPX_2 with 1,2-dimetallic derivatives of alkanes, and by cyclization of C-P-C units.[3] The stability of phosphiranes improves with bulky substituents on the phosphorus atom, but they remain photolytically labile[4] and subject to [2+1] cycloreversion,[5] retro-electrocyclization,[6] and ring-chain rearrangement.[7]

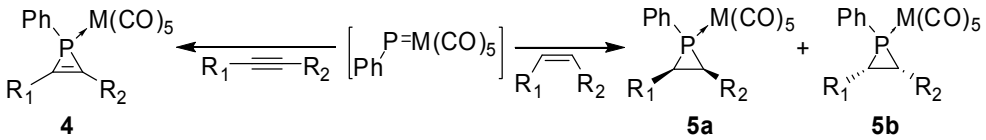


Scheme 1. Synthesis of uncomplexed phosphiranes

Phosphiranes with a transition metal complex coordinated to the phosphorus center are intrinsically more stable. Several methods have been reported to obtain these complexed heterocycles. A popular method is the addition of a transient electrophilic phosphinidene R–P=M(CO)$_5$ (M = Cr, Mo, W) to the C=C bond of a suitable substrate. The most widely used precursor 7-phosphanorbornadiene complex **2** generates this phosphinidene through thermal cheletropic elimination.[8] Recently, a new precursor was developed, 3*H*-3-benzophosphepine complex **3** (Scheme 2),[9] that offers more flexibility in the choice of the transition metal complex. It has also been shown that transient R$_2$N–P=Fe(CO)$_4$, generated from Collman's reagent, adds to double bonds, albeit only to terminal ones.[10] Still other precursors have been reported that are capable of transferring (trapping) electrophilic phosphinidene complexes by addition to olefins and alkynes to generate isomeric phosphiranes **5** and phosphirenes **4** (Scheme 3). Azaphosphirene complexes[11] and 1-amino-phosphirane and -phosphirene complexes[12] have also been used to generate electrophilic phosphinidenes.



Scheme 2. Two phosphinidene precursors



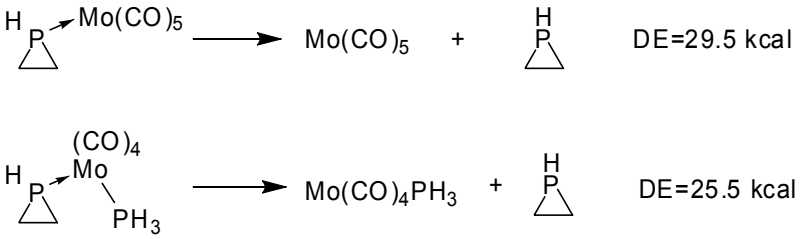
Scheme 3. Addition reactions of a phosphinidene transition metal complex

There are only a few methods to remove a transition metal complex from the three-membered heterocycles, but none works reliably and consistently for all systems, possibly in part due to the perceived sensitivity of the uncomplexed products. Decomplexation of the $W(CO)_5$ group has been explored most. One approach is the selective oxidation with iodine to weaken the W-P bond followed by ligand exchange with *N*-methylimidazole.[13] In a variation of this method, pyridinium tribromide is used for the oxidation of W(0) to W(II) and 2,2'-bipyridine for the displacement of the phosphine.[14] The use of this method for the decomplexation of sensitive compounds like phosphiranes is very limited, and to the best of our knowledge, only one such example has been reported.[15]

Direct exchange for a bidentate diphosphine ligand has been reported to work only for very stable phosphiranes, as high temperatures (~150 °C) are needed.[16a] With this method, phospholes and 1-chlorophosphirenes can also be demetallated.[16b,c] Trimethylamine N-oxide has been reported as a reagent for oxidative decomplexation of a P-$W(CO)_5$ complex to the corresponding phosphoryl compound.[17] Finally, the electrochemical decomplexation of phosphine-$W(CO)_5$ complexes has been reported for phosphole compounds.[18]

Photodissociation of the transition metal group has received little attention, probably because the reverse process is used to exchange CO for phosphine ligands in metal carbonyl complexes.[19] However, TD-DFT

calculations on $(C_2H_4)PH-Cr(CO)_5$ and $H_3P-Cr(CO)_5$ suggested that photochemical decomplexation may be a viable option.[20] PB88/TZP calculations also indicated that the phosphirane-$Mo(CO)_5$ complex weakens by 4 kcal/mol on replacing a CO for a PH_3 ligand.



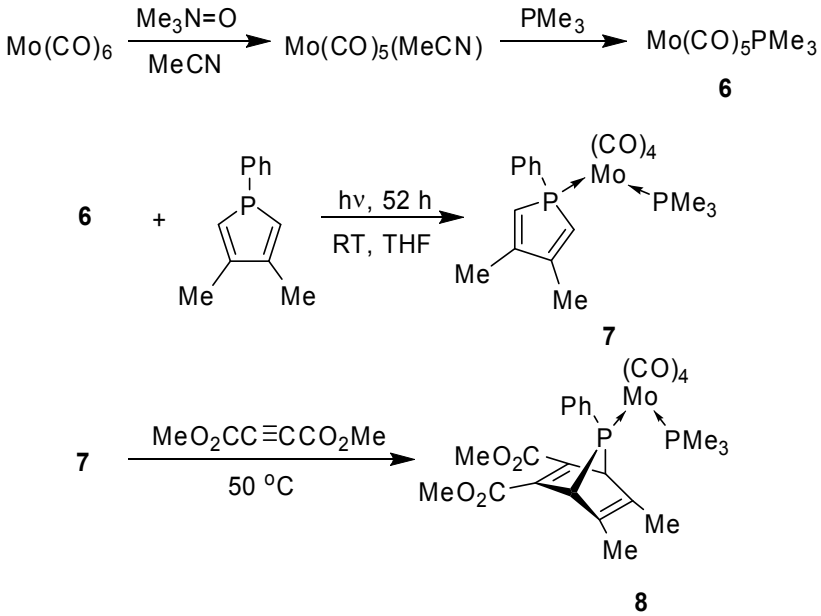
To expand the access to metal-free phosphorus heterocycles, which have potential in asymmetric catalysis,[21] we report on a decomplexation procedure that is based on pressurized reactions in a CO atmosphere. As proof of principle we use as substrates phosphirene and phosphirane molybdenum carbonyl complexes carrying one additional phosphine ligand.

3.3 Results and Discussion

The first step is the synthesis of phosphinidene precursor **8**, based on the 7-phosphanorbornadiene unit, having a $Mo(CO)_4PMe_3$ group coordinated to the phosphorus atom. Next this phosphinidene will be added to olefins and alkynes. Such phosphiranes coordinated to a transition metal carbonyl complex carrying an additional phosphine ligand are rare. We are aware of only a phosphirane Fe-complex with a bidentate diphosphine ligand[22] and bidentate phosphine Mo-complexes in which the second phosphine is linked to the phosphirane ring.[23] Finally, the demetallation from the phosphiranes and phosphirenes will be discussed.

3.3.1 Synthesis of phosphinidene precursor 8

This phosphanorbornadiene derivative can be obtained by cycloaddition of an acetylene derivative and 3,4-dimethylphosphole-$Mo(CO)_4PMe_3$ complex **7**. The synthesis of **7** was pursued first by the addition of both phosphorus ligands, 1-phenyl-3,4-dimethylphosphole and PMe_3, to *cis*-$Mo(CO)_4(piperidine)_2$, but surprisingly this reaction yielded mostly bis-trimethylphosphine complex cis-$Mo(CO)_4(PMe_3)_2$. Sequential addition, starting with the phosphole followed by PMe_3, gave mixtures of phosphine complexes with cis-$Mo(CO)_4(PMe_3)_2$ as the major product.



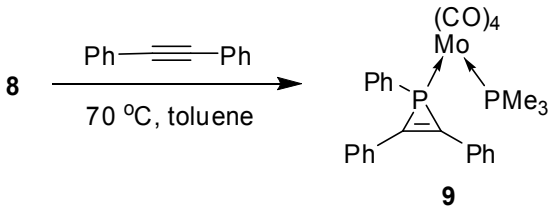
Scheme 4. Synthesis of a novel phosphinidene precursor

A more successful procedure started with the synthesis of $Mo(CO)_5PMe_3$ **6** (75% yield) from $Mo(CO)_6$ by oxidation with trimethylamine *N*-oxide, followed by replacement of the in-situ-formed acetonitrile complex with trimethylphosphine. Exchange of a *cis*-CO ligand for 1-

phenyl-3,4-dimethylphosphole by UV-irradiation in THF gave the desired Mo-complex **7** (61% yield). Its ^{31}P NMR spectrum shows doublets (^{2}J(P,P) = 24.5 Hz) at +33.6 ppm for the phosphole ligand and at -15.3 ppm for the PMe_3 ligand. Diels-Alder reaction of **7** with dimethyl acetylenedicarboxylate yielded phosphinidene precursor **8** in 50% isolated yield (Scheme 4).

3.3.2 Phosphinidene Additions

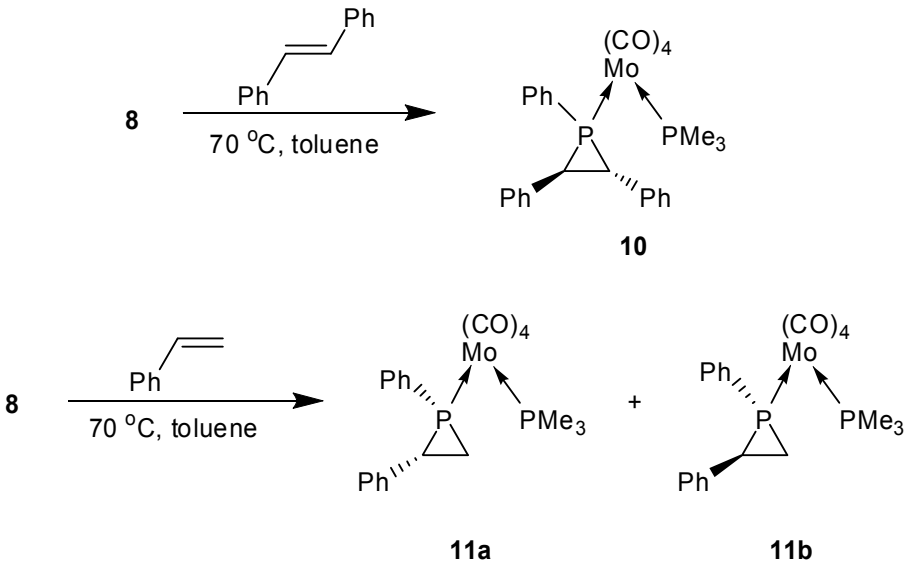
Heating a toluene solution of phosphanorbornadiene complex **8** and diphenylacetylene at 70 °C results in the rapid addition of transient $PhP{=}Mo(CO)_4PMe_3$ to the C≡C bond to give the Mo-complexed phosphirene **9** in 39% yield (Scheme 5). This yield is slightly higher than the 29% yield reported for the addition of transient $PhP{=}Mo(CO)_5$, which is generated at 120 °C.[14] Generally, because of the stronger W-P bond, higher yields are obtained with tungsten phosphinidene complexes. Only very recently was a higher yield of 66% reported by using a benzophosphepine phosphinidene precursor (Scheme 2, M = Mo) at 75-80 °C.[9] However, we could not use this precursor because it lacks the additional PMe_3 ligand. The ^{31}P NMR resonance at -130.0 ppm is normal for a Mo-complexed phosphirene and that at -14.2 ppm for PMe_3 is similar to that of **8**; the ^{2}J(P,P) coupling constant of 32.4 Hz is normal for *cis*-diphosphine compounds.



Scheme 5. Synthesis of a phosphirene complex

The reaction of **8** with the C=C bond of *trans*-stilbene gave phosphirane complex **10**, but in low isolated yield (21%) due to product

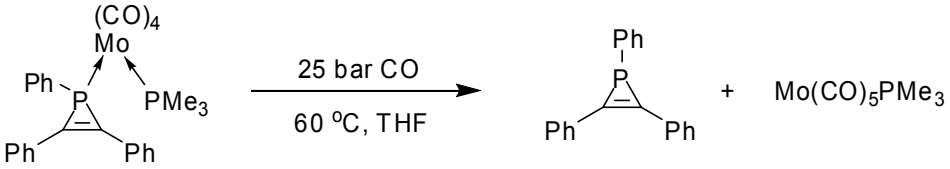
decomposition during the reaction. Reaction of **8** with styrene resulted in the formation (51%) of a mixture of diastereomeric phosphiranes **11a** and **11b** (ratio 8:1) in which the $Mo(CO)_4PMe_3$ group is oriented respectively *anti* and *syn* to the phenyl substituent of the ring. The products could be separated by crystallization. The *anti* assignment of the major isomer is based on steric considerations as we were unable to grow suitable crystals for an X-ray crystal structure determination. Addition reactions to sterically more hindered alkenes, such as $Ph_2C{=}CH_2$ and *t*BuCH=CH_2 did not result in the formation of the desired phosphiranes. The ^{31}P NMR resonances of phosphirane complexes **10** (-89.5) and **11** (**a** -125.6; **b** -124.6) are similar to those of the $W(CO)_5$-complexes.[24] During the synthesis of **10** and **11** small amounts (< 5%) of the demetallated products were detected by their ^{31}P NMR resonances at -147 and -182 ppm, respectively. This suggests that mild heating may suffice to remove the transition metal group, which can be captured by CO under pressurized condition.



Scheme 6. Synthesis of phosphirane complexes

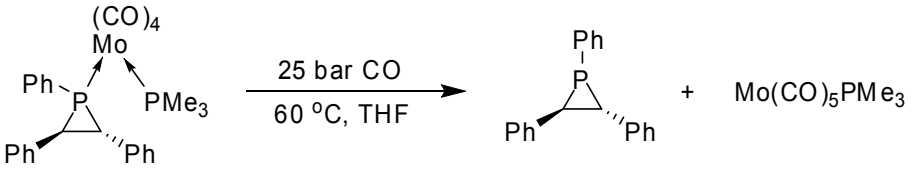
3.3.3 Demetallation

The decomplexation of Mo-complex 9 occurs already at 60 °C to give over 48 hours the known free triphenylphosphirene **12**[15] in 94% isolated yield. Also the metal fragment is nearly quantitatively recovered as $Mo(CO)_5PMe_3$ (**6**) and can be reused in the synthesis of **8**. Removal of the transition metal group results in a 57 ppm shielding of the ^{31}P NMR chemical shift to -187.4 ppm. Free PMe_3 is not observed under the reaction conditions.

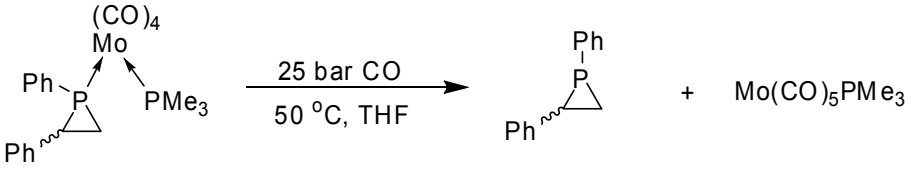


9 **12** **6**

Scheme 7. Phosphirene decomplexation



10 **13** **6**

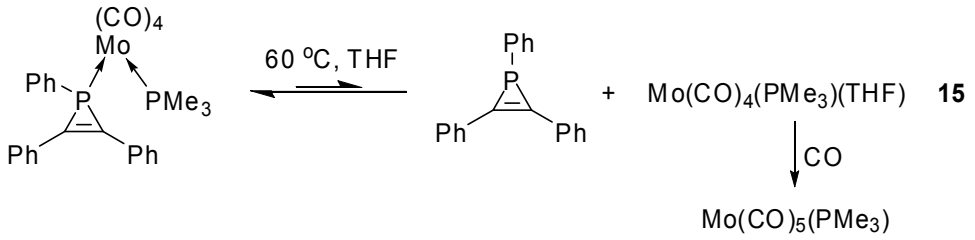


11 **14** **6**

Scheme 8. Phosphirane decomplexation

Decomplexation of phosphirane **10** occurs likewise, but more care has to be exercised because of the sensitivity of the product to oxygen. Thus,

heating **10** ($\delta(^{31}P)$ –88.6 and –15.2 ppm, $^{2}J(P,P)$ 30.5 Hz) at 60 °C for 24 hours resulted in the near quantitative formation of free triphenyl-phosphirane **13** ($\delta(^{31}P)$ = –147.5 ppm) and $Mo(CO)_5PMe_3$ ($\delta(^{31}P)$ = –15.1 ppm). Also complex **11a** ($\delta(^{31}P)$ –125.6 and –14.6 ppm, $^{2}J(P,P)$ = 31.4 Hz) is converted at 60 °C to the free phosphirane (**14**, $\delta(^{31}P)$ –182.2 ppm) without isomerization. Monitoring the decomplexing of a **11a,b** mixture by ^{31}P NMR shows the formation of both phosphirane isomers **14** ($\delta(^{31}P)$ = –182.2 and –197.2 ppm) in the same ratio. Phosphirane **14** is thermally not very stable and undergoes slow degradation at 60 °C, thereby lowering the observed ratio of phosphirane to $Mo(CO)_5PMe_3$. Decomplexation of phosphiranes **10** and **11** was performed on a 5 mg scale. Due to the instability of the free phosphiranes, we reduced the reaction time by increasing the ratio of CO to phosphirane complex. In our experimental setup, suited for monitoring the reactions, this could only be achieved by reducing the amount of phosphirane complex to 5 mg. An autoclave and higher CO pressures are recommended for larger scale reactions.

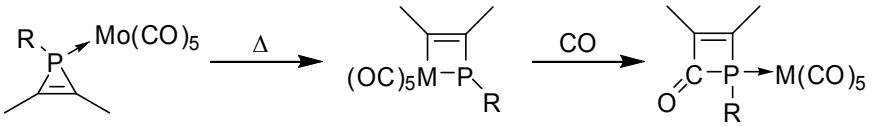


Scheme 9. Possible reaction path for decomplexation

A possible explanation for the mild decomplexation of the $Mo(CO)_4PMe_3$ group at 60 °C could be the existence of an equilibrium between the complex of the three-membered heterocycle and its free form. Indicative is the rapid formation of small amounts of the decomplexed phosphirene and phosphiranes at the slightly higher temperature of 80 °C. The presence of CO dissolved in the reaction mixture is apparently capable

of capturing the possible intermediate **15**, thereby driving the decomplexation to completion.

The reaction is remarkable as thermolysis of $M(CO)_5$-complexed phosphirene **16** (M = Cr, Mo, W) has been reported by Mathey *et al.*[14] to give ring enlargement via carbonylation of a phosphorus-carbon bond (Scheme 10). The mechanism involves intermediate 1-phospha-2-metallacyclobutene **17**, which is carbonylated in modest yield (8-43%) to phosphete complex **18**. We did not observe this reaction with the $Mo(CO)_4PMe_3$ complexed phosphirene, which illustrates that the PMe_3 ligand contributes to the weakened coordination of the transition metal to the heterocycle.



16 **17** **18**

Scheme 10. Thermolysis of phosphirene-transition metal complexes

3.4 Conclusions

Transient phosphinidene complex Ph-P=$Mo(CO)_4PMe_3$ is generated at only 70 °C from its 7-phosphanorborandiene precursor and adds to olefinic and acetylenic bonds to form $Mo(CO)_4PMe_3$ complexed phosphiranes and phosphirenes, respectively. The phosphine ligand reduces the P=Mo bond strength as compared to the all carbonyl complex. The transition metal group is readily removed under mild CO pressure by selective replacement of the 3-membered PCC rings for CO. Byproduct $Mo(CO)_5PMe_3$ of this reaction is used photochemically to generate $Mo(CO)_4PMe_3$ complexed phosphole **7**, from which phosphinidene precursor **8** is obtained in a mild Diels-Alder reaction with dimethyl acetylenedicarboxylate.

3.5 Experimental

All experiments were performed under an atmosphere of dry nitrogen. Solids were dried in vacuum and liquids were distilled under N_2 prior to use. Toluene was distilled over sodium, and THF was dried by successive distillation over $LiAlH_4$ and sodium/benzophenone. CH_2Cl_2 was dried over P_2O_5. 1-Phenyl-3,4-dimethylphosphole[25] was prepared according to literature procedures. NMR spectra were recorded on a Bruker WM 250 spectrometer (^1H, ^{13}C), internally referenced to residual solvent resonances and 85% H_3PO_4 (^{31}P) as external standard. IR spectra were recorded on a Mattson 6030 Galaxy FT-IR spectrophotometer and high-resolution mass spectra (HR-MS) on a Finnigan Mat 900 spectrometer (EI, 70 eV). Fast Atom Bombardment (FAB) mass spectrometry was carried out using a JEOL JMS SX/SX 102A four-sector mass spectrometer, coupled to a JEOL MS-MP9021D/UPD system program. Samples were loaded in a matrix solution (3-nitrobenzyl alcohol) on to a stainless steel probe and bombarded with Xenon atoms with an energy of 3KeV. During the high resolution FAB-MS measurements a resolving power of 10,000 (10% valley definition) was used. Column chromatography was performed using silica gel (Silia*Flash* P60, Silicycle) using indicated solvents as determined with TLC. Thin-layer chromatography was performed using silica gel plates (Silica-gel 60 F254 plates, Merck). Melting points were measured on samples in unsealed capillaries and are uncorrected.

Synthesis of (trimethylphosphine)pentacarbonylmolybdenum 6

$Mo(CO)_6$ (3.00 g, 11.4 mmol) and $Me_3N^+O^- \cdot 2H_2O$ (1.27g, 11.5 mmol) were added to 50 mL of a 1:1 mixture of dichloromethane and acetonitrile. The reaction mixture was stirred for 1.5 h at room temperature. A 11.4 mL portion of 1M PMe_3 in toluene was slowly added to the reaction mixture. Stirring was continued for 1.5 h at room temperature. Evaporation to dryness and column chromatography (silica gel, pentane/dichloromethane 5:1) gave **6** (2.80 g, 79%) as a white solid.

^{31}P NMR ($CDCl_3$) δ −15.3 (s, $P(CH_3)_3$). The ^{1}H and ^{13}C NMR data are identical to those in ref. [26]

Synthesis of *cis*-(trimethylphosphine)(3,4-dimethyl-1-phenylphosphole)-tetracarbonylmolybdenum 7

$Mo(CO)_5PMe_3$ (**6**) (2.40 g, 8.01 mmol) was dissolved in 200 mL dry THF. Nitrogen was bubbled through the solution and 1.65 g (9.00 mmol) 1-phenylphosphole was added. The reaction mixture was stirred for 44 h while being irradiated with a high pressure Philips Hg lamp (0.9 A, Type 93110E). UV-light was filtered out using a 0.1 cm thick glass plate. Evaporation to dryness, column chromatography (silica gel, pentane/dichloromethane 5:1) and recrystallization from dichloro-methane/hexane gave 2.32 g (61%) of **7** as yellow crystals.

M.p: 69-70 °C; ^{31}P NMR ($CDCl_3$) δ −15.3 (d, ^{2}J(P,P) = 24.5 Hz; $P(CH_3)_3$), 33.6 (d, ^{2}J(P,P) = 24.5 Hz; phosphole); ^{1}H NMR ($CDCl_3$) δ 1.28 (d, ^{2}J(H,P) = 7.0 Hz; 9H, $P(CH_3)_3$), 2.10 (s, 6H, CH_3), 6.52 (d, ^{2}J(H,P) = 36.0 Hz; 2H, C=CH), 7.28-7.54 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 17.3 (d, ^{3}J(C,P) = 9.7 Hz; CH_3), 20.5 (dd, ^{1}J(C,P) = 22.6 Hz; ^{3}J(C,P) = 2.0 Hz; $P(CH_3)_3$), 128.4 (d, ^{3}J(C,P) = 9.4 Hz; *m*-Ph), 129.3 (d, ^{4}J(C,P) = 2.0 Hz; *p*-Ph), 131.0 (dd, ^{1}J(C,P) = 34.3 Hz; ^{3}J(C,P) = 8.1 Hz; P-C=), 131.1 (d, ^{2}J(C,P) = 12.0 Hz; *o*-Ph), 133.2 (dd, ^{1}J(C,P) = 33.1 Hz; ^{3}J(C,P) = 2.8 Hz; *ipso*-Ph), 148.8 (d, ^{3}J(C,P) = 7.7 Hz; $CHCCH_3$), 209.8 (dd, ^{2}J(C,P) = 10.4 Hz; ^{2}J(C,P) = 9.2 Hz; *cis*-CO), 214.6 (dd, ^{2}J(C,P) = 23.9 Hz; ^{2}J(C,P) = 8.4 Hz; *trans*-CO), 215.0 (dd, ^{2}J(C,P) = 22.1 Hz; ^{2}J(C,P) = 9.0 Hz; *trans*-CO); IR (CH_2Cl_2) ν(CO) = 2017 (w), 1903 (vs), 1880 (sh) cm^{-1}; HR-MS Calcd. for $C_{19}H_{22}O_4P_2Mo$ 474.0047, Found 474.0046

Synthesis of *cis*-(trimethylphosphine)(5,6-dimethyl-2,3-bis(methoxy-carbonyl)-7-phenyl-7-phosphanorbornadiene)tetracarbonylmolybdenum 8

A mixture of complex **7** (1.60 g, 3.39 mmol) and dimethyl acetylenedicarboxylate (10 mL, 82.6 mmol) was stirred at 50 °C for 22 h.

Column chromatography (silica gel, starting with pentane and gradually converting to dichloromethane) gives a yellow solid. Recrystallization from dichloromethane/hexane resulted in 1.02 g (49%) of **8** as orange crystals.
M.p. 120–121 °C (decomp.); ^{31}P NMR ($CDCl_3$) δ –14.6 (d, ^2J(P,P) = 27.7 Hz; $P(CH_3)_3$), 253.2 (d, ^2J(P,P) = 27.7 Hz; 7-phosphanorbornadiene); ^{1}H NMR ($CDCl_3$) δ 1.34 (d, ^2J(H,P) = 6.8 Hz; 9H, $P(CH_3)_3$), 2.02 (s, 6H, CH_3), 3.63 (s, 6H, CO_2CH_3), 3.85 (d, ^2J(H,P) = 3.5 Hz; 2H, =C–CH–C=), 7.14–7.30 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 15.9 (d, ^3J(C,P) = 1.7 Hz; CH_3), 21.5 (dd, ^1J(C,P) = 23.1 Hz; ^3J(C,P) = 2.5 Hz; $P(CH_3)_3$), 51.6 (s, OCH_3), 60.5 (dd, ^1J(C,P) = 14.1 Hz; ^3J(C,P) = 2.3 Hz; P–*C*H–C=), 127.9 (d, ^3J(C,P) = 6.3 Hz; *m*-Ph), 128.6 (d, ^2J(C,P) = 9.3 Hz; *o*-Ph), 128.7 (s, *p*-Ph), 137.3 (d, ^1J(C,P) = 17.4 Hz; *ipso*-Ph), 142.2 (d, ^2J(C,P) = 3.5 Hz; *C*=*C*–CH_3), 145.6 (d, ^2J(C,P) = 17.4 Hz; *C*=*C*–CO_2CH_3), 165.2 (d, ^3J(C,P) = 2.2 Hz; *C*O_2CH_3), 208.7 (dd, ^2J(C,P) = 10.4 Hz; ^2J(C,P) = 8.1 Hz; *cis*-CO), 214.1 (dd, ^2J(C,P) = 11.5 Hz; ^2J(C,P) = 2.5 Hz; *trans*-CO), 214.5 (dd, ^2J(C,P) = 9.2 Hz; ^2J(C,P) = 4.5 Hz; *trans*-CO); IR (CH_2Cl_2) ν(CO) = 2021 (w), 1913 (vs), 1889 (sh) cm^{-1}; HR-MS (FAB+) Calcd. for $C_{25}H_{28}O_8P_2Mo$ 616.0313, found 616.0296

Synthesis of *cis*-(trimethylphosphine)(1,2,3-triphenylphosphirene)tetracarbonylmolybdenum 9

A mixture of **8** (500 mg, 0.81 mmol) and diphenylacetylene (470 mg, 2.64 mmol) dissolved in 15 mL dry toluene was stirred at 70 °C for 5.25 h. Column chromatography (silica gel, pentane/dichloromethane 7:3) and recrystallization from dichloromethane/hexane gave **9** (190 mg, 39%) as yellow crystals.
Mp 143–144 °C; ^{31}P NMR ($CDCl_3$) δ –130.0 (d, ^2J(P,P) = 32.4 Hz; phosphirene), –14.2 (d, ^2J(P,P) = 34.2 Hz; $P(CH_3)_3$); ^{1}H NMR ($CDCl_3$) δ 1.24 (d, ^2J(H,P) = 6.8 Hz; 9H, $P(CH_3)_3$), 7.43–7.93 (m, 15H, Ph); ^{13}C NMR ($CDCl_3$) δ 20.7 (dd, ^1J(C,P) = 22.7 Hz; ^3J(C,P) = 2.8 Hz; $P(CH_3)_3$), 127.9 (d, ^3J(C,P) = 6.3 Hz; *m*-Ph), 128.6 (d, ^2J(C,P) = 9.3 Hz; *o*-Ph), 128.2–31.4 (m, Ph), 140.0 (d, ^1J(C,P) = 6.1 Hz; *ipso*-Ph), 209.7 (dd, ^2J(C,P) = 10.5 Hz; ^2J(C,P) = 11.4

Hz; *cis*-CO), 213.9 (dd, ^2J(C,P) = 35.6 Hz; ^2J(C,P) = 8.9 Hz; *trans*-CO), 214.5 (dd, ^2J(C,P) = 23.3 Hz; ^2J(C,P) = 10.1 Hz; *trans*-CO); IR (CH_2Cl_2) ν(CO) = 2020 (w), 1908 (vs), 1882 (sh) cm^{-1}; HRMS (70eV) m/z (%)572 (2) [M^+]. 516 (1) [M^+-2CO], 488 (1) [M^+-3CO], 460 (4) [M^+-4CO], 384 (6) [M^+-4CO&$P(CH_3)_3$], 314 (18) [$PhPMo(CO)_4$], 286 (22) [M^+-$Mo(CO)_4P(CH_3)_3$],178 (100) [PhCCPh]; calculated mass for $C_{27}H_{24}O_4P_2Mo$: 572.02039, found: 572.01932;

Synthesis of *cis*-(trimethylphosphine)(1,2,3-triphenylphosphirane)tetracarbonylmolybdenum 10

A mixture of **8** (500 mg, 0.81 mmol) and *trans*-stilbene (517 mg, 2.87 mmol) dissolved in 15 mL dry toluene was stirred at 70 °C for 5.75 h. ^{31}P NMR spectroscopy showed that the precursor-to-product ratio was ca. 1:1. Column chromatography (silica gel, pentane/dichloromethane 7:3) and recrystallization from dichloromethane/hexane gave **10** (99 mg, 21%) as colorless crystals. Mp 127-128 °C; ^{31}P NMR ($CDCl_3$) δ -89.5 (d, ^2J(P,P) = 30.0 Hz; phosphirane), -15.3 (d, ^2J(P,P) = 30.0 Hz; $P(CH_3)_3$); ^1H NMR ($CDCl_3$) δ 1.19 (d, ^2J(H,P) = 6.9 Hz; 9H, $P(CH_3)_3$), 3.45 (dd, ^2J(H,P) = 3.1 Hz; ^3J(H,H) = 10.0 Hz; 1H, P-CHPh), 3.85 (dd, ^2J(H,P) = 7.5 Hz; ^3J(H,H) = 10.0 Hz; 1H, P-CHPh) 7.00-7.50 (m, 15H, Ph); ^{13}C NMR ($CDCl_3$) δ 20.7 (dd, ^1J(C,P) = 23.0 Hz; ^3J(C,P) = 2.7 Hz; $P(CH_3)_3$), 33.4 (dd, ^1J(C,P) = 20.4 Hz; ^3J(C,P) = 1.6 Hz; P-CHPh), 35.7 (dd, ^1J(C,P) = 21.9 Hz; ^3J(C,P) = 3.9 Hz; P-CHPh), 126.2-133.2 (m, Ph), 135.7 (d, ^3J(C,P) =7.0 Hz; *ipso*-Ph), 137.4 (s; *ipso*-Ph), 208.7 (t, ^2J(C,P) = 10.3 Hz; *cis*-CO), 214.2 (m; *trans*-CO); IR (CH_2Cl_2) ν(CO) = 2022 (w), 1913 (vs), 1881 (sh) cm^{-1}; HRMS (70eV) m/z (%) 574 (2) [M^+], 394 (3) [$PhPMo(CO)_4P(CH_3)_3$], 366 (4) [$PhPMo(CO)_3P(CH_3)_3$], 338 (4) [$PhPMo(CO)_2P(CH_3)_3$], 310 (7) [$PhPMo(CO)P(CH_3)_3$], 288 (10) [M^+-$Mo(CO)_4P(CH_3)_3$], 179 (100) [PhCHCHPh]; Calc. for $C_{27}H_{26}O_4P_2Mo$: 574.03601, Found: 574.03559;

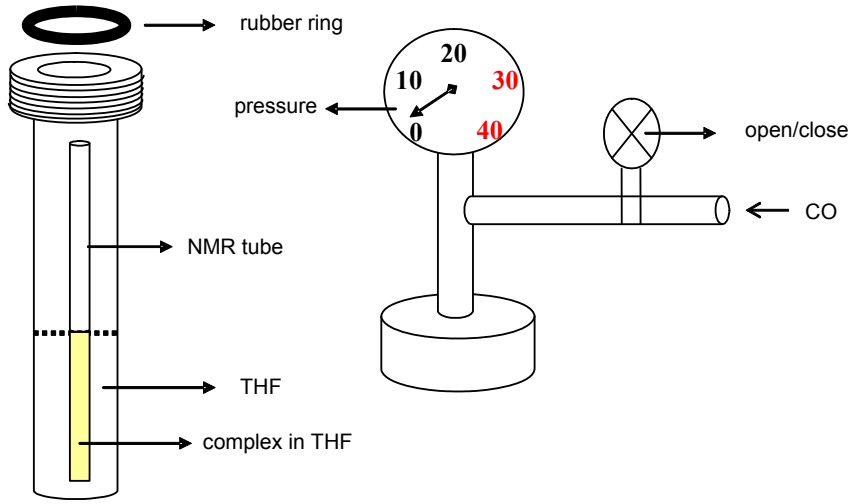
Synthesis of *cis*-(trimethylphosphine)(1,2-diphenylphosphirane) tetracarbonylmolybdenum 11

A mixture of **8** (400 mg, 0.65 mmol) and styrene (0.75 ml, 6.50 mmol) dissolved in 15 mL dry toluene was stirred at 70 °C for 9.5 h. Column chromatography (silica gel, pentane/dichloromethane 7:3) and recrystallization from dichloromethane/hexane gave **11** (165 mg, 51%) as colorless crystals. Two diastereomers were formed in a 8 to 1 ratio. The two isomers can be separated by slow recrystallization from dichloromethane/hexane. The minor isomer was not obtained in pure form.

Major isomer: Mp 66-67 °C; ^{31}P NMR ($CDCl_3$) δ -125.6 (d, ^2J(P,P) = 31.4 Hz; phosphirane), -14.6 (d, ^2J(P,P) = 31.4 Hz; $P(CH_3)_3$); ^{1}H NMR ($CDCl_3$) δ 1.34 (d, ^2J(H,P) = 6.8 Hz; 9H, $P(CH_3)_3$), 1.74-1.82 (m, 1H, P-CH), 2.22-2.32 (m, 1H, P-CH), 2.89-2.96 (m, 1H, P-CH), 6.81-6.85 (m; 2H, Ph), 7.00-7.15 (m, 8H, Ph); ^{13}C NMR ($CDCl_3$) δ 14.3 (dd, ^1J(C,P) = 16.1 Hz; ^3J(C,P) = 2.0 Hz; PCH_2), 21.0 (dd, ^1J(C,P) = 22.9 Hz; ^3J(C,P) = 2.8 Hz; $P(CH_3)_3$), 30.8 (dd, ^1J(C,P) = 20.8 Hz; ^3J(C,P) = 3.6_Hz; P-CHPh), 126.1-133.4 (m, Ph), 133.8 (d, ^1J(C,P) = 15.9 Hz; *ipso*-Ph), 136.0 (d, ^2J(C,P) = 5.5 Hz; *ipso*-Ph), 209.0 (t, ^2J(C,P) = 10.4 Hz; *cis*-CO), 214.5 (dd, ^2J(C,P) = 24.3 Hz, ^2J(C,P) = 11.0 Hz; *trans*-CO), 214.5 (dd, ^2J(C,P) = 34.3 Hz, ^2J(C,P) = 8.8 Hz; *trans*-CO); IR (CH_2Cl_2) ν(CO) = 2021 (w), 1907 (vs), 1889 (sh) cm^{-1}; HR-MS Calcd. for $C_{21}H_{22}O_4P_2Mo$ 498.0047, Found 498.0043;

minor isomer: ^{31}P NMR ($CDCl_3$) δ -124.6 (d, ^2J(P,P) = 31.4 Hz; phosphirane), -14.9 (d, ^2J(P,P) = 31.4 Hz; $P(CH_3)_3$);

Schematic view of equipment for decomplexation reactions:



Decomplexation of phosphirene-$Mo(CO)_4PMe_3$ 9

A NMR tube was charged with phosphirene complex **9** (89 mg, 0.15 mmol) and 1.5 mL dry THF. The tube was pressurized at 25 bar CO and heated for 48 h at 60 °C. ^{31}P NMR showed complete conversion of the complex to the free phosphirene (see Figure 1). The reaction mixture was filtered over a short silica gel column. Recrystallization from pentane gave **12** (40 mg. 94%); m.p. 76-77 °C (lit. 73 °C) ^{31}P NMR ($CDCl_3$) δ = -187.2 (s); ^{1}H NMR ($CDCl_3$) δ = 7.19-7.25 (m, 3H; Ph), 7.40-7.51 (m, 8H; Ph), 7.84-7.88 (m, 4H; Ph). The spectroscopic data are identical to those of ref [15]

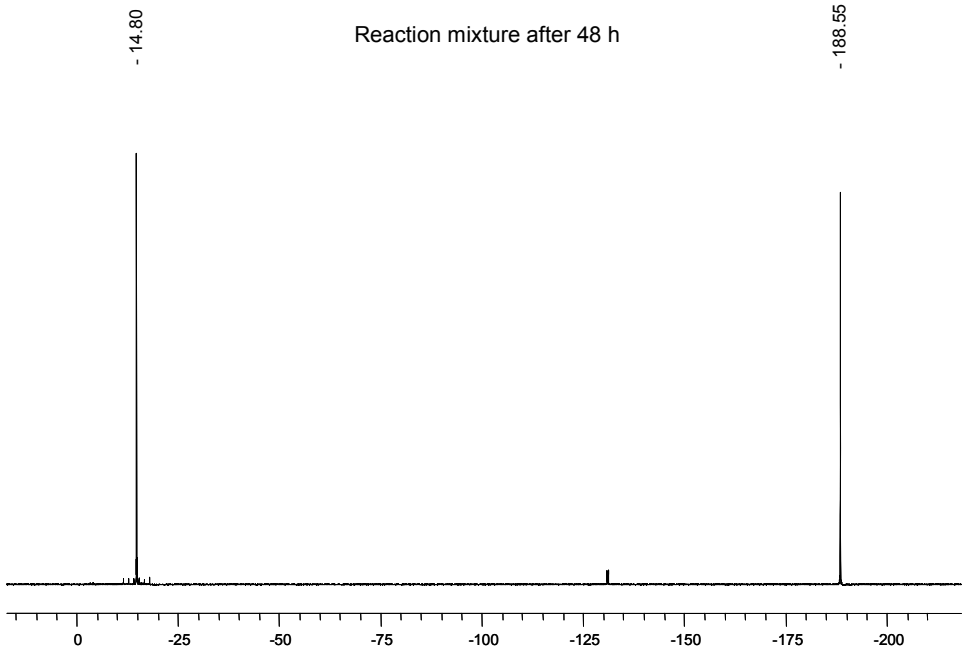


Figure 1. ^{31}P NMR spectrum of phosphirene decomplexation

Decomplexation of phosphirane-$Mo(CO)_4PMe_3$ 10

A NMR tube was charged with phosphirane complex **10** (5 mg, 9 μmol) and 0.75 mL dry THF. The tube was pressurized at 25 bar CO and heated for 24 h at 60 °C. ^{31}P NMR showed complete conversion of the complex to the free phosphirane **13**. Upon prolonged heating, thermal degradation of the phosphirane was observed.

^{31}P NMR [intensity] (THF) δ = -147.5 (s, phosphirane) [0.995], -15.1 (s, $Mo(CO)_5PMe_3$) [1.000]

Decomplexation of phosphirane-$Mo(CO)_4PMe_3$ 11a

A NMR tube was charged with phosphirane complex **11a** (5 mg, 10 μmol) and 0.75 mL dry THF. The tube was pressurized at 25 bar CO and heated for 10 h at 60 °C. ^{31}P NMR showed clean conversion of the complex to the

free phosphirane. The conversion of complex to free phosphine was 1 : 3, but without formation of byproducts. Upon prolonged heating, thermal degradation of the phosphirane **14** was observed.

^{31}P NMR [intensity] (THF) δ = −182.2 (s, free phosphirane) [1.00], −125.7 (d, ^{2}J(P,P) = 31.4 Hz; complex) [0.35], −14.9 (s, $Mo(CO)_5PMe_3$) [1.05], −14.5 (d, ^{2}J(P,P) = 31.4 Hz; complex) [0.37].

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Chapter 4

Acetylene Substituted Phosphine Oxides:

Building Blocks for Macrocycles

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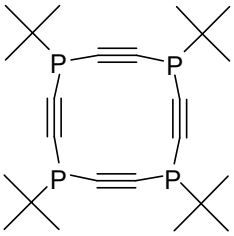
4.1 Abstract

Phosphorus-based macrocycles with acetylenic scaffolds were built from acetylene substituted phosphine oxides that were formed from diisopropylphosphoramidic dibromide **3** and an acetylenic Grignard reagent. The four- and six-edged macrocycles **15** and **16**, in which the *i*Pr$_2$NP(O) units are connected through 1,3-butadiyne rods, were obtained from the monosilylated derivative of *i*Pr$_2$NP(O)(C$_2$H)$_2$ (**7**) by multiple acetylene coupling reactions under oxidative Hay conditions. Reaction of *i*Pr$_2$NP(O)(Br)$_2$ (**3**) with lithiated 1,2-bisethynylbenzene gave a mixture of *cis* and *trans* monocyclic diphosphine oxide **18**. An X-ray crystal structure determination of the *trans* isomer shows the ring structure to adopt a puckered form.

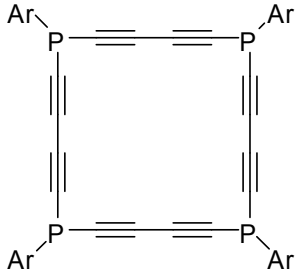
4.2 Introduction

Acetylenic scaffolds have been heavily pursued over the past decade, mainly because of their optoelectronic properties.[1] From the perspective of carbon networks, beautifully designed 1-, 2-, and 3-dimensional scaffolds have been prepared.[2] Remarkably, with the exception of sulfur-based molecules, heteroatoms have rarely been embedded in these rigid wires, rings, boxes, and cages. Especially in the context of the special P/C relationship,[3] it is surprising that hardly any attention has been paid to the incorporation of phosphorus atoms. Examples of their potential are the thiophene and pyridine conjugated phospholes, which possess optical and electrochemical properties.[4]

Only a few examples are known of phosphorus containing carbon skeletons. In 1990 Scott *et al.*[5] reported on alkynyl conjugated organophosphorus ring structures such as **1**. Later, Märkl *et al.*[6] reported on the synthesis of cyclic ethynylphosphanes, like **2**.



1



2

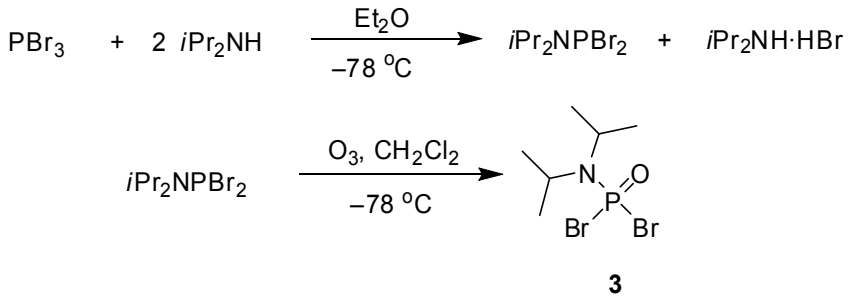
In the present study we use ethynylphosphine oxides as starting point for the synthesis of cyclic P/C-frames to simplify the product handling. These are commonly generated from air-sensitive ethynylphosphanes by peroxide oxidation.[7] Instead, we use a *bis*-ethynylphosphine oxide with an amine substituent, which has the advantage over P-alkyl and P-aryl groups in that it enables further functionalization.[8]

4.3 Results and Discussion

The synthesis and manipulation of the building blocks will be discussed first, followed by an evaluation of the Grignard and oxidative Hay coupling reactions to construct the P/C-macrocycles. A P/C-ring structure obtained from 1,2-bisethynylbenzene and diisopropylphosphoramidic dibromide is described in the final section.

4.3.1 Building blocks

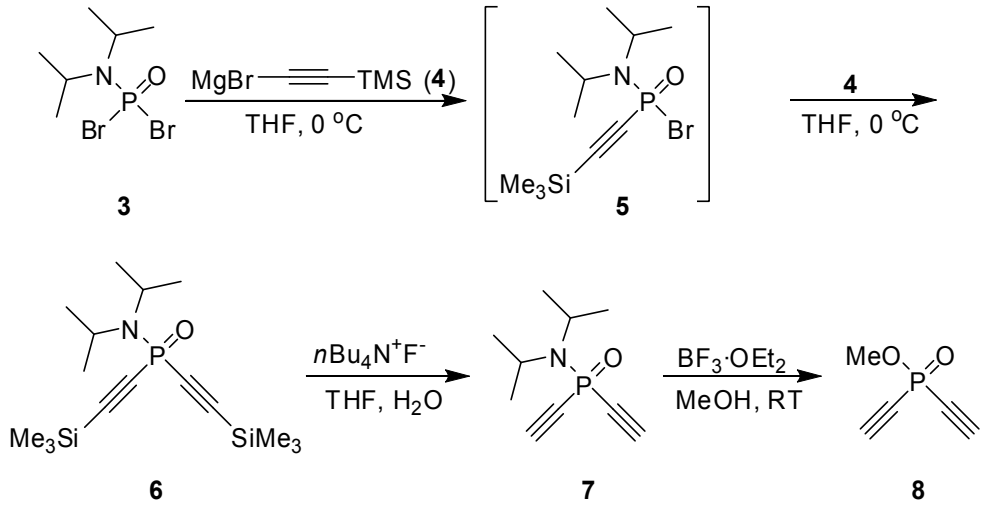
Diisopropylphosphoramidic dibromide (*i*Pr$_2$NP(O)Br$_2$) (**3**), a potential corner unit of the P/C-rings, can be generated from the oxygen and moisture sensitive *i*Pr$_2$NPBr$_2$,[9] obtained from the addition of diisopropylamine to PBr$_3$ (85%), by reaction with ozone at -78 °C in dichloromethane (70%) as monitored by ^{31}P NMR spectroscopy (+174.3 → -34.1 ppm) for maximum conversion.



3

Scheme 1. Synthesis of iPr$_2$NP(O)Br$_2$ (**3**).

Replacing the bromines of **3** for acetylene units gives a potentially even better building block, but reaction with HC≡C–MgBr (2 equiv.) resulted in mostly black unidentified material and only in trace amounts of the dialkynylated phosphine oxide. Apparently, the Grignard reagent (or the product) is not stable under the reaction conditions. Using instead the silyl protected Grignard reagent BrMgC≡CTMS (**4**) gave indeed dialkynyl-phosphinic amide **6** (80%) via non-isolable mono-alkynylated intermediate **5** ($\delta(^{31}P)$ = –15 ppm) (Scheme 2). Purification of **6** by column chromatography with either silica gel or aluminum oxide led to partial desilylation,[7a] while tetrabutylammonium fluoride (TBAF) on silica in wet THF at –78 °C gave full conversion to **7** (68% isolated yield) (Scheme 2), which is a stable solid that can be kept for months when stored below 0 °C. Related building blocks such as sterically protected diethynylphosphanes and butadiynylphosphanes have been reported by Yoshifuji and co-workers.[10]



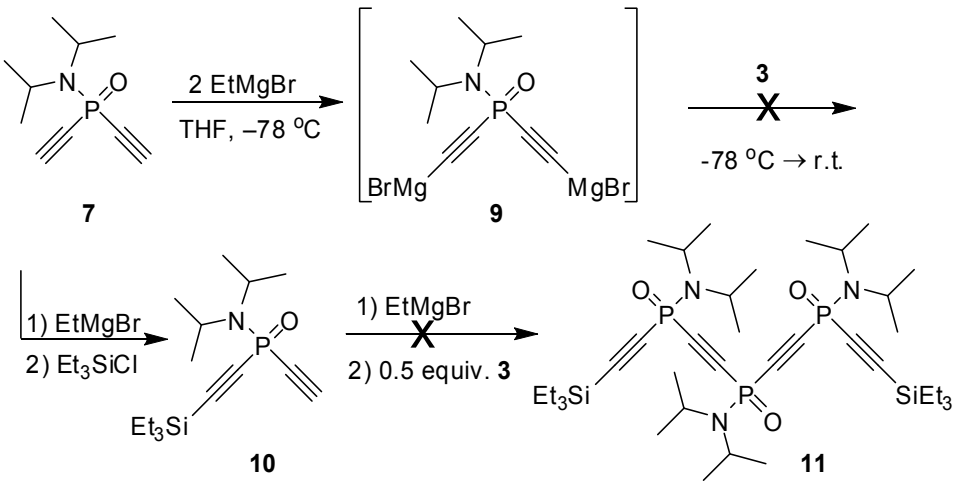
Scheme 2. Synthesis of phosphinic amide **7** and phosphinate **8**.

Whereas **7** did not hydrolyze with HCl(g)/Et_2O nor with conc. HCl[11], the amine substituent could be replaced by a methoxy group by reaction with $BF_3 \cdot OEt_2$ in methanol to give phosphinate **8** (50%) as a volatile light yellow liquid (Scheme 2).[12] ^{31}P NMR monitoring of the reaction showed the clean conversion of **7** (–21.5 ppm) to product **8** (–19.6 ppm). The presence of the MeO–group is evident from the δ(^{1}H) at 3.87 ppm (^3J(H,P) = 13.9 Hz) and δ(^{13}C) at 53.3 ppm (^2J(C,P) = 5.8 Hz). There are many methods to convert phosphinates into phosphinic chlorides, e.g., by PCl_5, $SOCl_2$, $COCl_2$,[13] enabling further substitution. Instead of dibromide **3** we also explored *i*$Pr_2NP(O)Cl_2$, synthesized from *i*Pr_2NPCl_2 by ozone oxidation[14] as precursor to **6**, but reaction with BrMg–C≡CTMS (**4**) required temperatures above 50 °C, causing degradation of the Grignard reagent.

4.3.2 Grignard Reactions

Our first approach was to use both building blocks **3** and **7** to form cyclic P/C–frames in a single step. Di–Grignard reagent **9** could be formed from **7** and EtMgBr (or *n*–BuLi), as the TMSCl quenching to **6** suggests, but

reaction with **3** at –78 °C → r.t. did not give the desired ring products. Instead, rapid polymerization occurred above –20 °C. ^{31}P NMR analysis showed the presence of some unreacted **7** in the reaction mixture. Since the same polymerization occurred in the absence of **3**, di-Grignard reagent **9** is apparently not stable under the reaction conditions and presumably reacts faster intermolecularly with a P=O group than with **3**. Likewise, reaction of a mono-Grignard reagent, generated from **10,** with **3** also resulted in black insoluble material instead of giving triphosphinoyl coupling product **11** (Scheme 3). **10** is obtained from the mono-anion of **7** by Et_3SiCl quenching, giving a mixture, separable by chromatography, of the product (53%), starting material (17%), and disilylated product (trace).[15]

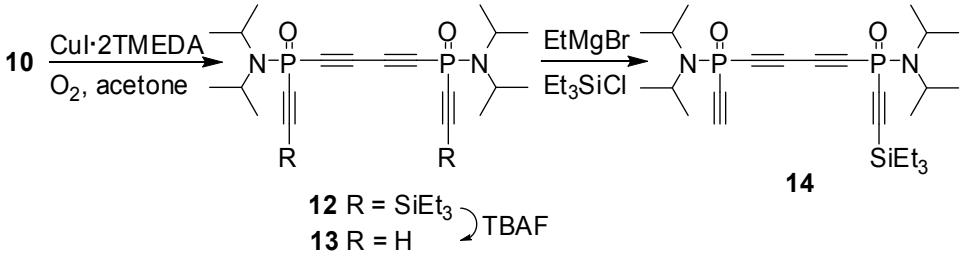


Scheme 3. Attempted Grignard condensations.

The unwanted behavior of the acetylenic phosphine oxides[16] suggests that the acetylide attacks the acetylenic P-atom rather than the P-Br bond of **3**, which relates to the dephosphinylation of *N*-diphenylphosphinyl aziridines by organometallic reagents like PhLi.[12]

4.3.3 Acetylene Self-Coupling Reactions

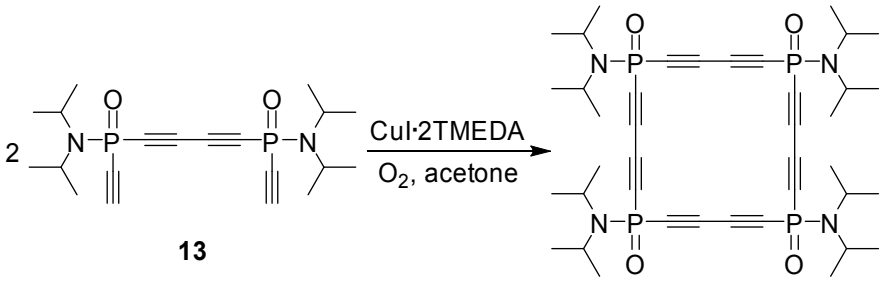
Our next approach was to use a single building block, ethynylphosphinic amide **10**, to form the P/C-cycles by intermolecular coupling of the acetylenic groups. Various coupling procedures may be considered such as the Glaser,[17] Englinton,[18] and Hay[19] reactions that are well known in acetylene scaffolding of carbon analogues. However, only the Pericàs modification of the oxidative Hay-coupling, which is also used to synthesize dialkoxybutadiynes from alkoxy-acetylenes,[20] gave coupling product **12** in 67% yield (Scheme 4). The protective silyl groups of **12**, which slowly degrades in $CDCl_3$, turning brown, were removed at -78 °C with TBAF on silica to give **13** (60%) that may exist in two diastereomeric (racemic and meso) forms. Hence, while two ^{31}P NMR chemical shifts would be expected,[6] the observed single one at -21.9 ppm may indicate that the difference between them is too small to detect.



Scheme 4. Oxidative Hay coupling of **10**

Cyclic products may be obtained from **13** by either a double oxidative Hay-coupling ('shot-gun' approach) or in a stepwise manner. The latter requires mono-silylation (**14**), coupling, deprotection, and cyclization steps. However, treating **13** with EtMgBr or *n*-BuLi at -78 °C → -30 °C followed by Et_3SiCl quenching gave **14** in only 13% yield as a moderately stable pale white solid ($\delta(^{31}P)$ = -23.2 ppm (Si-C≡C-P), -22.2 ppm

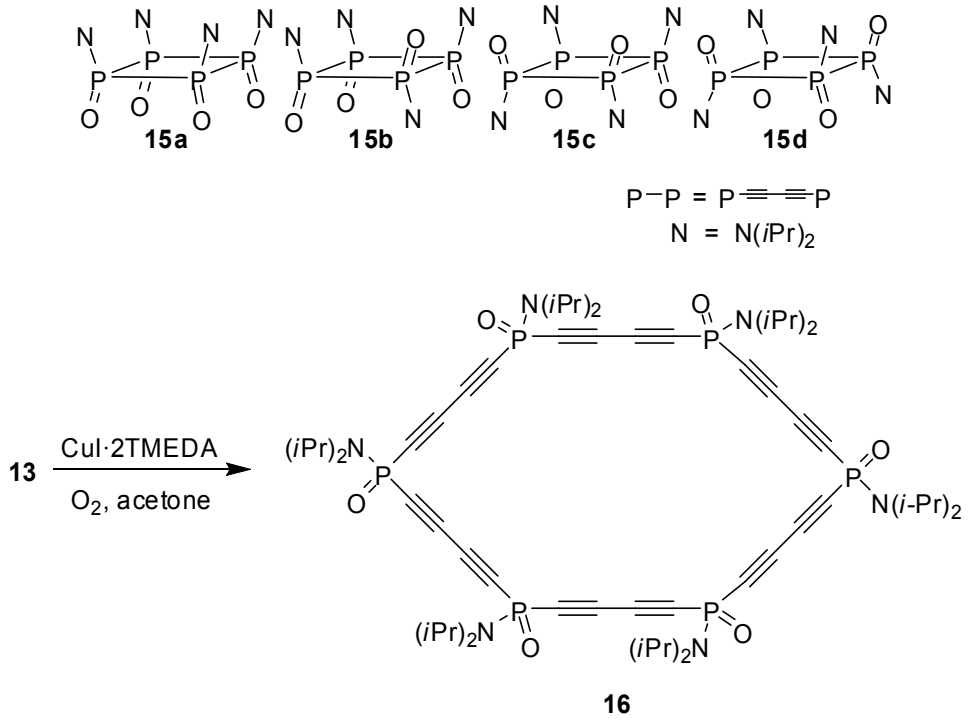
(HC≡C–P)), which makes the stepwise route impractical for the synthesis of macrocycles.



13 **15**

Scheme 5. Dimerization of **15** under oxidative Hay conditions

The *inter*molecular coupling of **13** proved to be more successful. Using the high dilution Pericàs modification of the oxidative Hay coupling gave two sets of products that could be isolated by chromatography over silica gel. The ^{1}H NMR spectra of both sets showed the absence of acetylenic proton resonances, thereby suggesting that cyclic products had been formed. Both sets of compounds are stable when obtained as solids but slowly decomposed in solution. The fraction (18%) that eluded first from the column (silica, ethyl acetate/hexane 2:1, R_f 0.63–0.73) showed four distinct ^{31}P NMR single resonances with different intensities, ($\delta(^{31}P)$ ($CDCl_3$) = –23.7 (18%), –23.9 (30%), –24.1 (19%), –24.2 (33%). High resolution mass spectrometry confirmed the mixture to consist of structure **15**. We were unable to separate the isomers by chromatographic techniques. Given that **13** may exist as 2 diastereomers, cross coupling may lead to 4 isomers that could display a total of 6 resonances in the ^{31}P NMR spectrum. Namely, isomer **15b** with the lowest symmetry has three non-equivalent phosphorus centers, while each of the other 3 isomers **15a**,**c**,**d** has four equivalent phosphorus centers.[6]

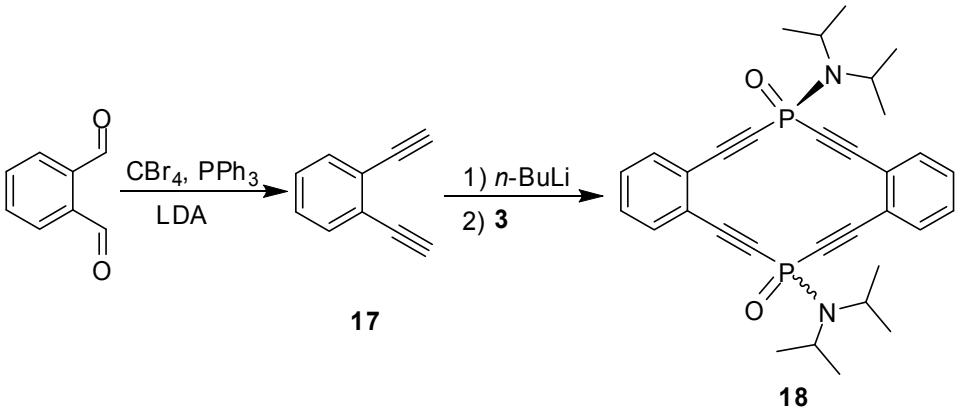


Scheme 6. Trimerization of **13** under oxidative Hay conditions

The second fraction (12%, R_f 0.38–0.48) showed a sharp singlet at δ(^{31}P) –24.1 ppm (16%) and broad unresolved resonances from –23.5 to –23.2 ppm (84%). High resolution mass spectrometry indicated the mixture to likely consist of isomers of trimer **16** (Scheme 6). We speculatively assign the singlet at –24.1 ppm to a single isomer with the phosphorus substituents being either all *cis* or all *trans*. Crystallization from a dichloromethane/hexane solvent mixture provided a 'hair'-like solid that slowly decomposed above 150 °C. Unfortunately, the 'hairs', with length up to 2 cm, were bent and twisted and not suitable for an X-ray crystal structure analysis. These type of hairs are also known as 'whiskers' and can be seen as a solid equivalent of nanotubes.[21]

4.3.4 Mixed Acetylene Coupling Reactions

Our final approach to the P/C-cycles is to couple **3** with a non-phosphorus containing linker. The objective is a more selective process than the self-coupling of **13** and to circumvent the ill-fated Grignard reaction of **7** with **3**. We decided for 1,2-bisethynylbenzene **17** that has, like **7**, an acute angle between the conjugated acetylenic groups and is readily accessible from commercially available *o*-phthalaldehyde.[22] Intermolecular cyclization of building blocks **3** and **17** proved indeed successful (Scheme 7). Thus, adding the di-acetylide of **17**, using *n*-BuLi, to a THF solution of **3** gave both the *cis* and *trans* isomers of cyclic diphosphine dioxide **18** (25%) in a 2:3 ratio as determined by integration of their ^{31}P NMR resonances (*cis* –20.4; *trans* –20.2).



Scheme 7. Synthesis of cyclic ethynylphosphine oxide **18**

The single crystal X-ray structure of the *trans*-isomer, shown in Figure 1, confirmed the formation of the cyclic structure. The pyramidal nature of the phosphorus centers (N1-P1-C1 106.37(14)°, O1-P1-C1 113.098(13)°) causes the ring to be puckered. This is reflected in the dihedral angles of 127.71(17)° for C1-P1-P2-C11 and 116.07(16)° for C20-P1-P2-C10. The acetylene bonds are only marginally bent (P1-C1-C2 178.4(3)°, C1-C2-C3 178.9(3)°). As expected, the aliphatic ring C-C bonds are shortened (C2-C3 1.435(5) Å) compared to regular sp^3-sp^3 C-C single bonds. The crystal

structure displays normal bond lengths for the C≡C triple bonds (C1–C2 1.206(4) Å) and aromatic phenyl bonds (C3–C4 1.390(4) Å and C3–C8 1.406(4) Å). The P–C (P1–C1 1.753(4) Å), P–N (P1–N1 1.630(3) Å) and P–O (P1–O1 1.464(2) Å) bond lengths are in the expected range. The sulfide and silane analogues have been reported. They were synthesized via reaction of 1,2-bisethynylbenzene with either bis(benzenesulfonyl)sulfide (for sulfurization) or dichlorophenylsilane (for silylation).[23] The reported crystal structures of these compounds differ considerably from that of phosphine oxide **18**. The silicon analogue was found to be almost planar, while the sulfur analogue was only slightly puckered.

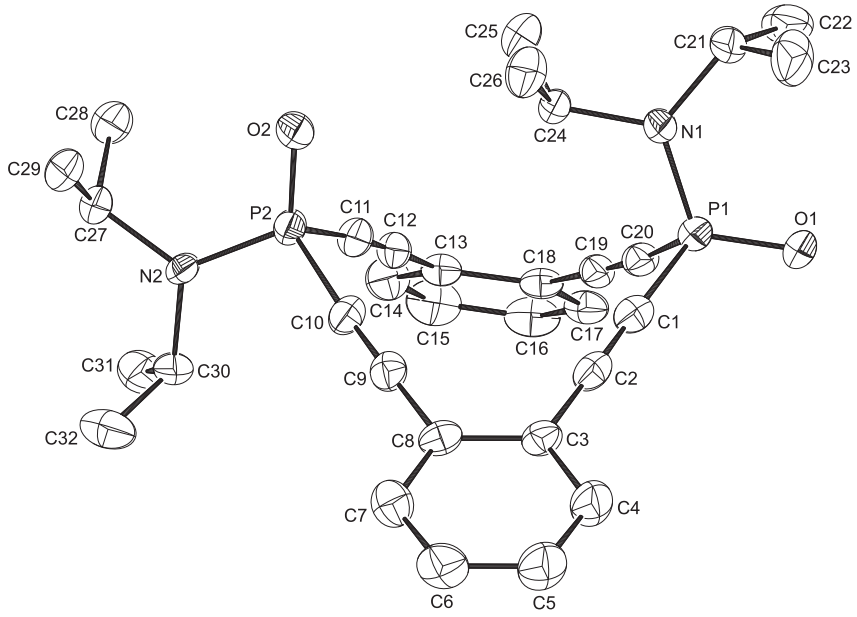


Figure 1. Displacement ellipsoid plot of *trans*-**18** in the crystal, drawn at the 50% probability level. Hydrogen atoms and disordered solvent molecules are omitted for clarity. Selected bond lengths [Å], angles and torsion angles [°]: P1–O1 1.464(2), P1–N1 1.630(3), P1–C1 1.753(4), P1–C20 1.760(3), P2–O2 1.468(2), P2–N2 1.622(2), P2–C10 1.753(3), P2–C11 1.765(3), C1–C2 1.206(4), C2–C3 1.435(5), C3–C8 1.406(4), C8–C9 1.442(4), C9–C10 1.202(4), C11–C12 1.206(4), C12–C13 1.434(5), C13–C18 1.402(4), C18–C19 1.442(4), C19–C20 1.201(4); O1–P1–N1 115.71(13), O1–P1–C1 113.09(13), N1–P1–C1 106.37(14), C1–P1–C20 100.73(15), P1–C1–C2 178.4(3), C1–C2–C3 178.9(3), C2– C3–C8 119.8(3), C3–C8–C9 119.4(3), C8–C9–C10

178.7(3), C9-C10-P2 176.2(3), O1-P1-N1-C21 8.7(3), C1-P1-N1-C21 135.2(2), C20-P1-N1-C21 -118.0(2), C2-C3-C8-C9 0.9(5);

4.4 Conclusions

We have demonstrated that amino containing acetylene substituted phosphine oxides can function as building blocks for the constructing of novel P/C-frames. The building blocks are readily accessible from **3** and acetylenic Grignard reagent **4**. Under oxidative Hay conditions dimeric unit **13**, obtained from monosilylated **10**, couples in modest yields to complex mixtures of the 20- and 30-membered macrocycles **15** and **16**. Coupling of phosphorus units **3** and **7** by way of a Grignard reaction did not lead to ring structures, but coupling of **3** with lithiated 1,2-bisethynylbenzene resulted in a *cis*, *trans* mixture of the 14-membered puckered macrocyclic system **18**.

4.5 Experimental

BrMg-C≡C-$SiMe_3$[24] and 1,2-bisethynylbenzene[22] were prepared according to literature procedures. All experiments, except for the oxidative Hay coupling reactions, were performed under an atmosphere of dry nitrogen. Solvents were purified, dried, and degassed by standard techniques. In reactions with wet THF, a few drops of H_2O were added to THF. NMR spectra were recorded (300K) on Bruker Advance 250 or MSL 400 spectrometers (^{31}P; 85% H_3PO_4) (^{1}H, ^{13}C, internally referenced to residual solvent resonances). High-resolution mass spectra (HRMS) were recorded on a Finnigan Mat 900 (EI, 70 eV). Fast Atom Bombardment (FAB) mass spectrometry was carried out using a JEOL JMS SX/SX 102A four-sector mass spectrometer, coupled to a JEOL MS-MP9021D/UPD system program. Samples were loaded in a matrix solution (3-nitrobenzyl alcohol) on to a stainless steel probe and bombarded with Xenon atoms with an energy of 3KeV. During the high-resolution FAB-MS measurements a resolving power of 10,000 (10% valley definition) was used. IR spectra were recorded on a

Mattson 6030 Galaxy spectrophotometer. Elemental analyses were performed by the Microanalytical Laboratory of the Laboratorium für Organische Chemie, ETH Zürich. Melting points were measured on samples in unsealed capillaries and are uncorrected.

Synthesis of $(i\text{Pr})_2\text{NPBr}_2$. PBr_3 (6.77 g, 25.0 mmol) was dissolved in 60 mL dry diethyl ether and cooled to –78 °C. Under fast stirring, $(i\text{Pr})_2\text{NH}$ (5.06 g, 50.0 mmol) was added in 30 minutes. The reaction mixture was allowed to warm to room temperature and stirred overnight after which it was filtered and the salts washed with diethylether. Evaporation of the solvents afforded a yellow oil. Distillation ($4\text{x}10^{-2}$ mbar) gave $(i\text{Pr})_2\text{NPBr}_2$ at 55–60 °C as a colorless liquid, which solidified upon cooling in a yield of 6.16 g (85%). The product is very air and moisture sensitive and slowly decomposes with a color change to yellow/orange, requiring storage below –20 °C. $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$, 27 °C) δ = 174.3 (s); ^1H NMR (250 MHz, $CDCl_3$, 27 °C) δ = 1.26 (d, ^3J(H,H) = 6.9 Hz, 12H; CH_3), 3.87–4.05 (m, ^3J(H,H) = 6.9 Hz, 2H; CH); $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$, 27 °C) δ = 22.9 (d, ^3J(C,P) = 8.6 Hz; CH_3), 50.8 (d, ^2J(C,P) = 13.7 Hz; CH); HR-MS Calcd. for $C_6H_{14}Br_2NP$ 288.9230, Found 288.9233 for the $^{79}Br^{79}Br$-isotope; this isotope is given because it doesn't interfere with the reference peak.

Oxidation of $(i\text{Pr})_2\text{NPBr}_2$ with ozone to $(i\text{Pr})_2\text{NP(O)Br}_2$ (3): $(i\text{Pr})_2\text{NPBr}_2$ (2.84 g, 9.76 mmol) was dissolved in 100 mL CH_2Cl_2 and cooled to –78 °C. Dry ozone was bubbled through the reaction mixture for several hours during which it slowly turned yellow/orange. The ^{31}P NMR spectrum indicated complete conversion of the starting material to a new product. Evaporation of CH_2Cl_2 and extraction with hexane (2×50 mL) afforded a solution of nearly pure $(i\text{Pr})_2\text{NP(O)Br}_2$ (**3**). Crystallization from hexane gave **3** (2.40 g, 80%) as a moisture sensitive white solid that required storage below –20 °C; slow decomposition occurred ≥ –20 °C with a color change to yellow/orange. M.p. 51–52 °C; $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$, 27 °C) δ = –

34.1 (s); ^{1}H NMR (250 MHz, $CDCl_3$. 27 °C) δ = 1.37 (d, ^{3}J(H,H) = 6.8 Hz 12H; CH_3), 3.68–3.80 (m, ^{3}J(H,P) = 30.3 Hz, ^{3}J(H,H) = 6.8 Hz, 2H; CH); ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$, 27 °C) δ = 21.7 (d, ^{3}J(C,P) = 2.4 Hz; CH_3), 49.8 (d, ^{2}J(C,P) = 5.3 Hz; CH); HR-MS Calcd. for $C_6H_{14}Br_2NOP$ 306.9159, Found 306.9169 (this is the most abundant $^{79}Br^{81}Br$ combination).

Synthesis of (*i*Pr)$_2$NP(O)(C≡CH)$_2$ 7: TMS-C≡C-MgBr (2 equiv., ~0.4 M in THF) was added dropwise at 0 °C to a solution of (*i*Pr)$_2$NP(O)Br_2 (950 mg, 3.1 mmol) in 10 mL THF and was slowly warm to room temperature; the ^{31}P NMR spectrum showed complete conversion to the product. The light-brown residual oil, obtained after solvent evaporation, was dissolved in 400 mL diethylether, washed with H_2O, and dried over $MgSO_4$. The crude product was dissolved in 50 mL of wet THF, cooled to 0 °C, and TBAF on silica (250 mg, 1–1.5 mol% fluoride per gram) was added. The reaction mixture was stirred for 1 hour and quenched with H_2O. Column chromatography (silica gel, ethyl acetate/hexane 1:1) yielded **7** (415 mg, 68%) as a light yellow solid. M.p: 134–135 °C; ^{31}P{^{1}H} NMR (101 MHz, $CDCl_3$, 27 °C) δ = -21.4 (s); ^{1}H NMR (250 MHz, $CDCl_3$, 27 °C) δ = 1.31 (d, ^{3}J(H,H) = 6.8 Hz, 12H; CH_3), 3.05 (d, ^{3}J(H,P) = 11.6 Hz, 2H; ≡C-H), 3.60–3.74 (m, ^{3}J(H,P) = 21.2 Hz, ^{3}J(H,H) = 6.8 Hz, 2H; N-CH); ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$, 27 °C) δ = 22.5 (d, ^{3}J(C,P) = 2.1 Hz; CH_3), 46.9 (d, ^{2}J(C,P) = 6.9 Hz; N-CH), 81.1 (d, ^{1}J(C,P) = 224.7 Hz; P-C≡), 88.3 (d, ^{2}J(C,P) = 41.5 Hz; ≡CH); HR-MS Calcd. for $C_{10}H_{16}NOP$ 197.0970, Found 197.0969.

Synthesis of MeO-P(O)(C≡CH)$_2$ (8): (*i*Pr)$_2$NP(O)(C≡CH)$_2$ **7** (195 mg, 1.0 mmol) was dissolved in a 1:1 mixture of MeOH and CH_2Cl_2 (40 mL) and cooled to 0 °C. $BF_3 \cdot Et_2O$ (600 μL, 4.0 mmol) was added at once and the reaction mixture was stirred at room temperature for 48 hours. The yellow solution was evaporated at reduced pressure and the resulting yellow oil was purified by column chromatography (silica gel, ethyl acetate). MeOP(O)(C≡CH)$_2$ (50 mg, 40%) was isolated as a volatile yellow liquid.

$^{31}P\{^{1}H\}$ NMR (101 Mhz, $CDCl_3$, 27 °C) δ = -19.7 (s); ^{1}H NMR (250 MHz, $CDCl_3$, 27 °C) δ =3.12 (d, ^{3}J(H,P) = 12.7 Hz, 2H; ≡C-H), 3.87 (d, ^{3}J(H,P) = 13.9 Hz, 3H; OCH_3); $^{13}C\{^{1}H\}$ NMR (63 MHz, $CDCl_3$, 27 °C) δ = 53.3 (d, ^{2}J(C,P) = 5.8 Hz; OCH_3), 76.2 (d, ^{1}J(C,P) = 259.4 Hz; P-C≡), 90.6 (d, ^{2}J(C,P) = 48.1 Hz; P-C≡*C*).

Synthesis of (*i*Pr)$_2$NP(O)(C≡CH)(C≡CSiEt$_3$) (10): (*i*Pr)$_2$NP(O)(C≡CH)$_2$ (3.00 g, 15.2 mmol) was dissolved in 150 mL THF and cooled to -78 °C. EtMgBr (1.05 equivalent,16 mL, 1M in THF) was added over a period of 15 min and the cloudy reaction mixture was stirred for an additional hour before warming it to -30 °C. Et_3SiCl (2.52 gram, 16.7 mmol) was added dropwise and the light yellow mixture was slowly warmed to room temperature. The solvent was evaporated and the yellow oil with white salts was filtrated over a short silica gel column using ethyl acetate/hexane (1:1). Column chromatography (silica gel, ethyl acetate/hexane 3:1) afforded mono-silylated **10** (2.50 g, 53%) followed by unreacted starting material **7** (500 mg, 17%). M.p 94-95 °C; $^{31}P\{^{1}H\}$ NMR 101 MHz, $CDCl_3$, 27 °C) δ = -22.3 (s); ^{1}H NMR ($CDCl_3$) δ = 0.64 (q, ^{3}J(H,H) = 7.9 Hz, 6 H; CH_2), 0.70 (t, ^{3}J(H,H) = 7.9 Hz, 9 H; CH_2-C*H*$_3$), 1.31 (d, ^{3}J(H,H) = 6.8 Hz, 12 H; CH-C*H*$_3$), 2.98 (d, ^{3}J(H,P) = 11.3 Hz, 1 H; ≡CH), 3.62-3.75 (m, ^{3}J(H,P) = 20.8 Hz, ^{3}J(H,H) = 6.8 Hz, 2 H; N-CH); $^{13}C\{^{1}H\}$ NMR (63 MHz, $CDCl_3$, 27 °C) δ = 3.7 (s, $SiCH_2$), 7.2 (s, CH_2*C*H$_3$), 22.2 (d, ^{3}J(C,P) = 1.6 Hz; CH-*C*H$_3$), 46.5 (d, ^{2}J(C,P) = 6.9 Hz; N-CH), 81.6 (d, ^{1}J(C,P) = 220.0 Hz; P-*C*≡CH), 87.1 (d, ^{2}J(C,P) = 40.7 Hz, ≡CH), 102.5 (d, ^{1}J(C,P) = 212.3 Hz; P-*C*≡CSi), 107.3 (d, ^{2}J(C,P) = 30.4 Hz, ≡CSi); HR-MS Calcd. for $C_{16}H_{30}NOPSi$ 311.1834, Found 311.1843.

Oxidative Hay coupling of 10 to 12: 10 (150 mg, 0.48 mmol) was dissolved in 10 mL of dry acetone and protected from light. A freshly prepared solution of 5 mol% CuI and 10 mol% TMEDA in 10 mL dry acetone was added. Air was bubbled through the clear green reaction mixture for 5 hours; dry acetone was added to compensate for solvent evaporation.

When the reaction stopped, as indicated by the blue color of the reaction mixture, another portion of 5 mol% CuI and 10 mol% TMEDA in dry acetone was added. The solvent was evaporated after full conversion was observed (as monitored by ^{31}P NMR) and the green/blue residue was dissolved in 10 mL diethyl ether, washed with water, and dried over $MgSO_4$. Column chromatography (silica gel, ethyl acetate/hexane 1:2) afforded **12** (100 mg, 67%) as a white solid.

M.p. 117–118 °C; $^{31}P\{^1H\}$ NMR (101 MHz, C_6D_6, 27 °C) δ = –23.9 (s); ^1H NMR (250 MHz, C_6D_6, 27 °C) δ = 0.45 (broad q, ^3J(H,H) = 7.5 Hz, 12 H; Si–CH_2), 0.91 (broad t, ^3J(H,H) = 7.5 Hz, 18 H; CH_2–CH_3), 1.35 (d, ^3J(H,H) = 6.7 Hz, 12 H; CH–CH_3), 1.44 (d, ^3J(H,H) = 6.6 Hz, 12 H; CH–CH_3), 3.60–3.80 (m, ^3J(H,P) = 21.4 Hz, ^3J(H,H) = 6.7 Hz, 4 H; CH); $^{13}C\{^1H\}$ NMR (63 MHz, C_6D_6, 27 °C) δ = 4.0 (s; Si–CH_2), 7.5 (s, Si–CH_2–CH_3), 22.0 (s, CH–CH_3), 22.6 (s, CH–CH_3), 46.9 (d, ^2J(C,P) = 7.0 Hz; N–CH), 79.6 (dd, ^2J(C,P) = 40.2 Hz, ^3J(C,P) = 7.4 Hz; P–C≡C–C≡), 82.0 (dd, ^1J(C,P) = 206.8 Hz, ^4J(C,P) = 2.2 Hz; P–C≡C–C≡), 103.5 (dd, ^1J(C,P) = 214.4 Hz, ^6J(C,P) = 3.8 Hz; P–C≡C–Si), 108.0 (dd, ^2J(C,P) = 30.4 Hz, ^7J(C,P) = 6.9 Hz; P–C≡C–Si); HRMS: Calcd. for $C_{32}H_{58}N_2O_2P_2Si_2$ 620.3512, Found 620.3519.

Desilylation of 12 to HC≡C–P(O)(N(*i*Pr)$_2$)–C≡C–C≡C–P(O)(N(*i*Pr)$_2$)–C≡CH (13): A solution of **12** (500 mg, 0.81 mmol) in 40 mL wet THF was cooled to –78 °C. TBAF on silica (110 mg, 1.0–1.5 mmol fluoride/gram) was added and the reaction mixture stirred at –78 °C for 2 hours, slowly turning black, after which it was quenched with a few drops of water. The black oil that resulted on evaporation of the solvent was purified by column chromatography (silica gel, ethyl acetate/hexane 1:1) to give **13** (190 mg, 60%) as a white crystalline solid.

M.p. > 140 °C (decomp.); $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$, 27 °C) δ = –21.9 (s); ^1H NMR (250 MHz, $CDCl_3$, 27 °C) δ = 1.31 (d, ^3J(H,H) = 6.8 Hz, 24 H; CH_3), 3.14 (d, ^3J(H,P) = 11.9 Hz, 2 H; ≡CH), 3.56–3.75 (m, ^3J(H,P) = 21.5 Hz, ^3J(H,H) = 6.8 Hz, 4 H; N–CH); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 27 °C) δ =

22.6 (multiple; CH_3), 47.1 (multiple; N–CH), 80.1 (multiple; P–*C*≡CH), 80.2 (multiple; P–*C*≡C–C≡), 80.3 (dd, ^2J(C,P) = 42.4 Hz, ^3J(C,P) = 7.8 Hz; P–C≡*C*–C≡), 89.8 (d, ^2J(C,P) = 42.8 Hz; P–C≡*C*H); HRMS Calcd. for $C_{20}H_{30}N_2O_2P_2$ 392.1783, Found 392.1765. Elem. anal.: Found C, 61.30; H, 7.70; N, 7.08. Calcd. for $C_{20}H_{30}N_2O_2P_2$: C, 61.22; H, 7.71; N, 7.14.

Monosilylation of 13 to 14: 13 (392 mg, 1.0 mmol) was dissolved in 10 mL THF and cooled to –78 °C. A solution of EtMgBr (1 mL, 1M in THF) was added dropwise in 30 min and the reaction mixture was stirred at –78 °C for 1 hour before allowing to warm to –30 °C where it was kept for 30 min and quenched with EtSiCl (0.2 mL, 1.2 mmol). The black residue that resulted after solvent evaporation was purified by column chromatography (silica gel, ethyl acetate/hexane 1:1) to give **14** as a pale white powder (50 mg, 13%) that slowly decomposed on exposure to light. Only a ^{31}P NMR spectrum was recorded. A pure ^{1}H NMR spectrum was not obtained because of residual solvents and decomposition products present in the sample.

$^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$, 27 °C) δ = –23.2 ppm (s, Si–C≡C–P), –22.2 ppm (s, H–C≡C–P).

Cyclization by Oxidative Hay coupling of 13 to 15 and 16: 500 mg (1.27 mmol) of **13** was dissolved in 250 mL of dry acetone and protected from light. A freshly prepared solution of 2 mol% CuI (12 mg) and 4 mol% TMEDA (18 μL) in 25 mL dry acetone was added at once. Upon addition of the catalyst, the color of the reaction mixture turned light-yellow. Air was bubbled through the reaction mixture for 10 hours. Every two hours, another portion of catalyst (1 mol% CuI and 2 mol % TMEDA in 10 ml dry acetone) was added. The reaction was followed by TLC. After full conversion of the starting material, the solvent was evaporated under reduced pressure and the dark brown residue purified by column chromatography (silica gel, ethyl acetate/hexane 1:1 and 2:1) to give two

sets of products with R_f 0.63–0.73 for **15** (91 mg, 18%) and R_f 0.38–0.48 for **16** (60 mg, 12%).

15 (mixture of isomers): M.p. > 175 °C (decomp.); $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$, 27 °C) δ = –23.1 (s, 18%), –23.3 (s, 30%), –23.5 (s, 19%), –23.6 (s, 33%); ^1H NMR (250 MHz, $CDCl_3$, 27 °C) δ = 1.33 (d, ^3J(H,H) = 6.7 Hz, 48H; CH_3), 3.61–3.78 (m, 8H; N–CH); $^{13}C\{^1H\}$ NMR (63 MHz, C_6D_6, 27 °C) δ = 20.2 (broad s, CH_3), 45.1 (broad, N–CH), 78.5–81.9 (P–*C*≡C & P–C≡*C*); HR–MS FAB+ [M+H] Calcd. for $C_{40}H_{57}N_4O_4P_4$ 781.3330 , Found 781.3336.

16 (single isomer isolated from crystallization in CH_2Cl_2/Hexane.): M.p. > 150 °C (decomp.); $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$, 27 °C) (mixture of isomers) δ = –24.1 (s, 16%), –23.3 (broad, 84%); ^1H NMR ($CDCl_3$) (single isomer) δ = 1.35 (d, ^3J(H,H) = 6.6 Hz, 72H; CH_3), 3.60–3.74 (m, ^3J(H,P) = 21.6 Hz, ^3J(H,H) = 6.6 Hz; 12H, N–CH); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 27 °C) (single isomer) δ = 22.4 (s, CH_3), 47.2 (d, ^2J(C,P) = 6.77 Hz; N–CH), C≡C resonances too weak to be observed; HR–MS FAB+ [M+H] Calcd. for $C_{60}H_{85}N_6O_6P_6$ 1171.4956 , Found 1171.5002.

The HRMS FAB spectrum indicates that a small amount of tetramer $C_{80}H_{112}N_8O_8P_8$ (M/Z 1561.7 (M+1)) is present in the second set of products after column chromatography.

Cyclization of 1,2-bisethynylbenzene (17) with $(i$Pr$)_2$NP(O)Br$_2$: 1,2-Bisethynylbenzene (380 mg, 3.0 mmol) was dissolved in 20 mL THF and cooled to –78 °C. *n*–BuLi (3.75 mL, 1.6M in hexanes) was added dropwise and the cloudy white solution was stirred for 1.5 hours at –78 °C after which it was added over a period of 30 minutes to a solution of $(i$Pr$)_2$NP(O)Br$_2$ (920 mg, 3.0 mmol) in 100 mL THF at –15 °C that turned from orange to dark green. After 1 hour at –15 °C the reaction mixture was warmed to room temperature and the solvent evaporated. Column chromatography (silica gel, ethyl acetate/hexane 1:1 to pure ethyl acetate) afforded pure *trans*–isomer **18** (120 mg, 15%) followed by the *cis*–isomer (80 mg, 10%) contaminated with 3 minor products, as UV–sensitive white

solids. Suitable crystals for X-ray diffraction of the *trans*-isomer were obtained by crystallization from ethyl acetate/hexane.

18 (*trans*-isomer): M.p 325 °C (decomp.); $^{31}P\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 27 °C) δ = -20.2 (s); ^{1}H NMR (250 MHz, $CDCl_3$, 27 °C) δ = 1.42 (d, ^{3}J(H,H) = 6.8 Hz, 24H; CH_3), 3.83-3.97 (m, ^{3}J(H,P) = 21.5 Hz, ^{3}J(H,H) = 6.8 Hz, 4H; N-CH), 7.38-7.43 (m, 4H; Ar), 7.50-7.55 (m, 4H; Ar); $^{13}C\{^{1}H\}$ NMR (63 MHz, $CDCl_3$, 27 °C) δ = 22.9 (d, ^{3}J(C,P) = 1.9 Hz; CH_3), 47.2 (d, ^{2}J(C,P) = 7.0 Hz; N-CH), 90.6 (d, ^{1}J(C,P) = 229.8 Hz; P-C≡), 95.9 (d, ^{2}J(C,P) = 42.8 Hz; P-C≡*C*), 124.4 (dd, ^{3}J(C,P) = 4.9 Hz, ^{4}J(C,P) = 2.2 Hz; *i*-Ph), 130.5 (s; Ph), 133.0 (d, ^{4}J(C,P) = 2.0 Hz; Ph); HR-MS Calcd. for $C_{32}H_{36}N_2O_2P_2$ 542.2252, Found 542.2259. Elem. anal.: Found C, 70.75; H, 6.54; N, 5.15. Calcd. for $C_{32}H_{36}N_2O_2P_2$: C, 70.84; H, 6.69; N, 5.16.

18 (*cis*-isomer): ^{31}P NMR (101 MHz, $CDCl_3$, 27 °C) δ = -20.4 (s) ^{1}H NMR (250 MHz, $CDCl_3$, 27 °C) δ = 1.42 (m, 24H; CH_3), 3.75-3.96 (m, 4H; N-CH), 7.30-7.46 (m, 4H; Ar), 7.48-7.64 (m, 4H; Ar).

Crystal structure data of 18: $C_{32}H_{36}N_2O_2P_2$ + disordered solvent, Fw = 542.57[*], colourless needle, 0.27 x 0.09 x 0.03 mm^3, monoclinic, P2/c (no. 13), a = 20.6225(3), b = 7.5377(1), c = 24.2849(5) Å, β = 94.7219(12)°, V = 3762.18(11) $Å^3$, Z = 4, D_x = 0.958 g/cm^3[*], μ = 0.14 mm^{-1}[*]. 35739 Reflections were measured on a Nonius Kappa CCD diffractometer with rotating anode (graphite monochromator, λ = 0.71073 Å) up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.56 $Å^{-1}$ at a temperature of 150 K. The reflections were corrected for absorption and scaled on the basis of multiple measured reflections with the program SADABS[25] (0.83-1.00 correction range). 5597 Reflections were unique (R_{int} = 0.0837). The structure was solved with Direct Methods[26] and refined with SHELXL-97[27] against F^2 of all reflections. The crystal structure contains large voids (1013 $Å^3$/unit cell) filled with disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the

SQUEEZE routine of the program PLATON,[28] accounting for 180 electrons / unit cell. Non hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were introduced in geometrically optimized positions and refined with a riding model. 351 Parameters were refined with no restraints. R1/wR2 [$I > 2\sigma(I)$]: 0.0553/0.1458. R1/wR2 [all refl.]: 0.0841/0.1566. S = 1.066. Residual electron density between -0.30 and 0.34 e/Å^3. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[28]

CCDC 625927 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

[*] Derived parameters do not contain the contribution of the disordered solvent molecules.

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Chapter 5

Phospha-Scorpionates by 'Click-chemistry' from Ethynylphosphine Oxides and Phenylazide. Novel N- and P-Ligand Systems

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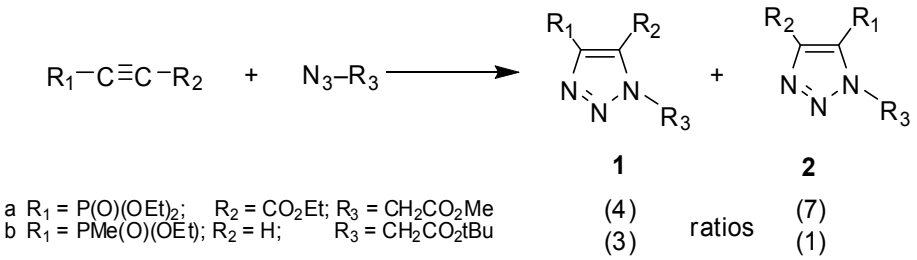
5.1 Abstract

Novel phosphine oxides (**6**) with one, two, and three 1,2,3-triazole substituents were obtained by a Cu(I)-catalyzed 'click' reaction between phenylazide and ethynyl substituted phosphine oxides (**5**). Reducing the triazole products **6a**/**c** with $PhSiH_3$ gave moderately air-stable phosphanes **7**. The ligating potential of these novel ligands was established by $W(CO)_5$-coordination to the P-atom to give **8** and by $RhCl_3$-coordination to the three N-atoms of **6c** to give **9**. X-ray crystal structures for both complexes are reported. A bimetallic $W(CO)_5/FeCl_3$ complex **11** was obtained by combining both types of coordination.

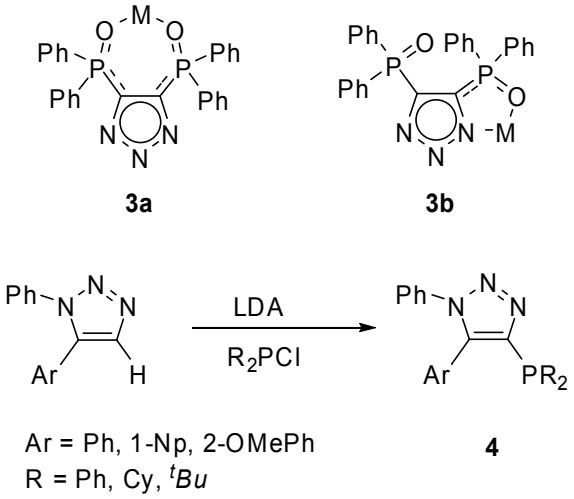
5.2 Introduction

Huisgen's 1,3-dipolar cycloaddition[1] between alkynes and azides, popularly known as the 'click'-reaction,[2] gives the biologically significant 1,2,3-triazole heterocycles, which are broadly applied in such diverse areas as synthesis[3], drug discovery[4], surface[5], polymer[6], and materials chemistry[7]. Both the 1,4- (**1**) and 1,5-disubstituted (**2**) derivatives are formed from various alkynes and azides at elevated temperatures, but the much milder copper(I)-catalyzed reaction, discovered in 2002, yields exclusively **1**.[8] This well-behaved reaction tolerates an exceptionally large variety of functional groups such as esters, acids, alkenes, alcohols, and amines, but hardly any is known with a phosphorus group. We are aware of two uncatalyzed azide additions to phosphinoylethynes (Scheme 1), namely the reaction of methyl azidoacetate reacting with ethyl(diethoxy-phosphinoyl)propyonate to give a 4:7 mixture of triazoles **1a** and **2a**,[9a] and the formation of **1b** and **2b** in a 3:1 ratio from ethynyl-methyl-phosphinic acid ethylester and *tert*-butylazidoacetate at elevated temperatures.[9b] These compounds have interesting O,O- and N,O-chelating properties as shown by Rheingold *et al.*[10] for bis(diphenylphosphinoyl)-1,2,3-triazole (**3a** and **3b**). The potential of phosphorus substituted 1,2,3-triazoles was

recently underscored by Zhang *et al.*[11] for the so-called ClickPhos **4**, synthesized by a substitution rather than by a cycloaddition reaction (Scheme 2), as a highly effective ligand in the Pd-catalyzed Suzuki-Miyaura coupling and amination reactions of aryl chlorides. To explore the accessibility and the potential of such heterocycles, we report in this study on the synthesis of novel phosphinoyl-triazoles from readily available phosphorus precursors. We will also demonstrate that these ligands readily complex with transition metal groups, including the formation of a phosphorus analogue of a homoscorpionate, to render new types of potential catalysts.



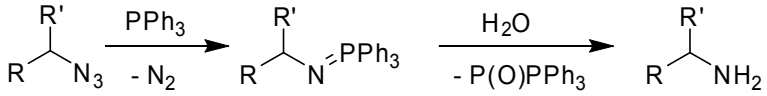
Scheme 1. Known triazole synthesis with phosphinoylethynes



Scheme 2. Synthesis of the ClickPhos ligand **4**

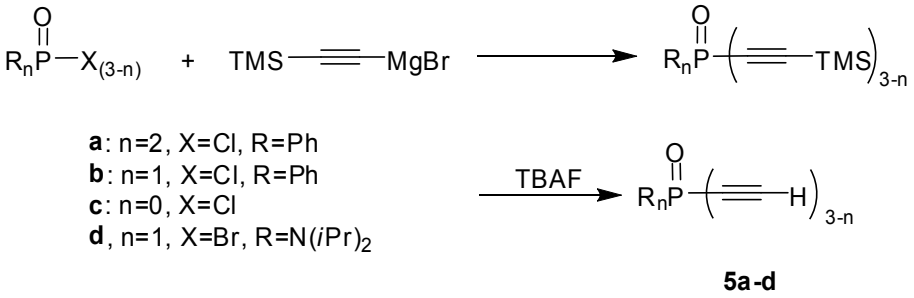
5.3 Results and Discussion

An obvious route to the desired phosphine substituted 1,2,3-triazoles might appear the direct cycloaddition of an azide to an alkynylphosphane, but these reagents are expected to give a Staudinger reaction instead, forming an amine and a phosphine oxide on hydrolysis of the intermediate phosphazene (Scheme 3).[12] Therefore, we opted to explore the phosphinoyl-ethynes **5** for the 1,3-cycloadditions in the expectation that the P=O bond of the phosphinoyl-triazoles can be reduced.



Scheme 3. Staudinger reaction between an azide and triphenylphosphine

The required phosphinoyl-ethynes **5**, having one, two, or three terminal acetylenic groups, can be obtained in good yield as stable solids from the reaction of chloro- and bromophosphine oxides with trimethyl-silyl-ethynyl magnesium bromide (TMS-C≡C-MgBr) followed by removal of the TMS group with tetrabutylammonium fluoride (TBAF) on silica or by chromatography over silica gel (Scheme 4). This route is preferred over literature procedures that either do not accommodate amine substituents, involve the use of acetylene gas, or proceed via the more difficult to handle alkynylphosphanes that require an oxidation step.[13a] The amine substituent provides a handle to vary the substituent on phosphorus. The ^{31}P NMR resonance of the products is in the expected range[13a] and show the large upfield shift that is expected on replacing a halogen for an alkynyl group (Table 1). The compounds can be stored for months at -30 °C without any sign of decomposition or polymerization.



Scheme 4. Synthesis of phosphinoyl-ethynes

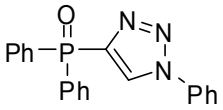
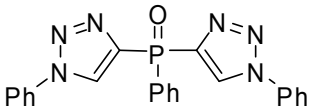
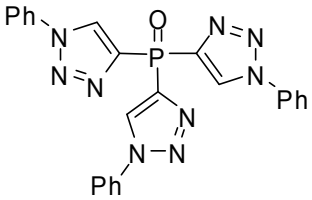
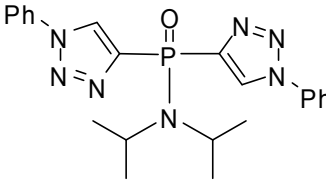
Table 1. Yields and ^{31}P NMR chemical shifts of phosphinoyl-ethynes

Reactant	Product	Yield (%)	δ(^{31}P) (ppm)
$Ph_2P(O)Cl$	$Ph_2P(O)-C\equiv CH$ **5a**	81	9.5 [13a]
$PhP(O)Cl_2$	$PhP(O)(C\equiv CH)_2$ **5b**	54	-19.5
$P(O)Cl_3$	$P(O)(C\equiv CH)_3$ **5c**	55	-56.8 [13a,b]
$(iPr)_2NP(O)Br_2$	$(iPr)_2N-P(O)(C\equiv CH)_2$ **5d**	68	-21.4

Of the many available procedures[8,14,15] to execute the Cu-catalyzed 'click' reaction of **5** with phenylazide we chose that of Rostovtsev *et al.*[8] in which the reaction is performed in water with *t*-butanol as co-solvent at room temperature over a 12-24 hr period, with Cu(I) as the catalyst, generated by sodium ascorbate mediated in situ reduction of Cu(II). This very mild reaction indeed afforded the novel 1,4-substituted 1,2,3-triazoles **6** (Table 2) with remarkable ease in > 70% isolated yield as high-melting white or light yellow solids. Not surprisingly, their ^{31}P NMR resonances are

deshielded with respect to the phosphinoyl-ethynes **5**. No 1,5-substituted derivatives were identified in the spectra of the crude reaction mixtures.

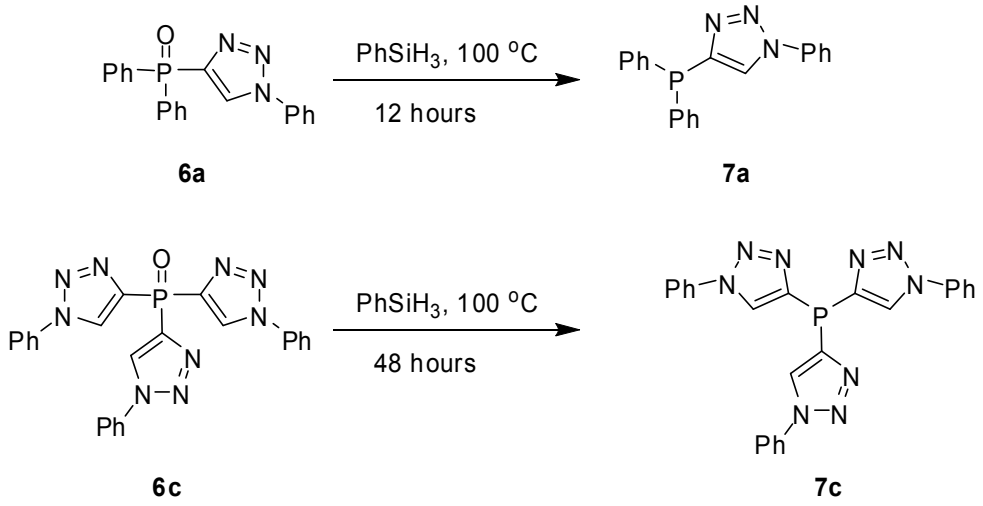
Table 2. Synthesis of 1,4-disubstituted 1,2,3-triazoles.[a]

Reactant	Product	Yield (%)	$\delta(^{31}P)$ (ppm)
5a	 **6a**	72	17.4
5b	 **6b**	74	5.3
5c	 **6c**	73	-5.7
5d	 **6d**	72	7.8

[a] 1 mol% of $CuSO_4$ and 10 mol% of sodium ascorbate was used for **6a,b** and 2 and 20 mol%, respectively, for **6c,d**.

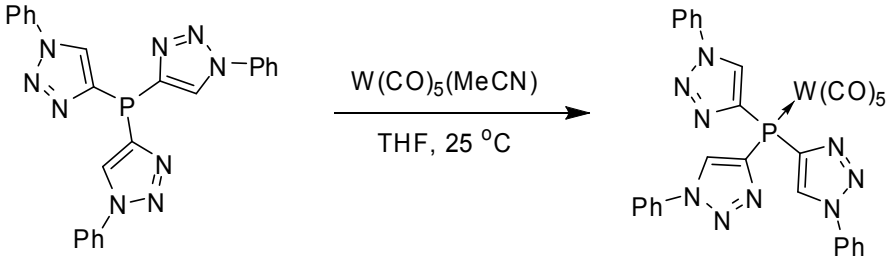
The P=O group of these very stable novel triazole substituted phosphine oxides **6** can be reduced conveniently with phenylsilane without

formation of side products. For example, heating **6a**,**c** in $PhSiH_3$ at 100 °C results cleanly in the corresponding phosphanes **7a**,**c** as monitored by ^{31}P NMR spectroscopy, which shows large upfield shifts for the phosphanes with very small ^1J(C,P) coupling constants (e.g., −32.7 (^1J(C,P) 6.7 Hz) for **7a** versus 17.4 (^1J(C,P) 142.3 Hz) for **6a**). The products **7** are readily isolated in > 90% as white solids by evaporation of $PhSiH_3$ and flash chromatography.



Scheme 5. Reduction of phosphine oxides **6** to phosphanes **7**

Phosphanes **7** with their aromatic N-heterocyclic substituents may have potential as novel P-ligand systems. A variety of P,N ligands are known with a pyridyl[16] or phthalazyl[17] residue. For example, 2-$PyPPh_2$, which is closely related to **7a**, is an excellent ligand for the Pd-catalyzed methoxycarbonylation of propyne to methyl metacrylate.[18] To demonstrate the ligating ability of the novel phosphanes we reacted **7c** with $W(CO)_5$[MeCN] at room temperature to form yellow solid tungsten complex **8** in 86% isolated yield, which has its ^{31}P NMR resonance at -42.3 ppm with a ^1J(P,W) coupling constant of 257.8 Hz.



7c **8**

Scheme 6. Complexation of phosphine **7c** to $W(CO)_5$

A X-ray single crystal structure determination (see Figure 1) of complex **8** revealed that the N-atoms in the crystal are rotated to the outer rim of the molecule. The triazole rings are essentially flat. Each of the 3 phenyl rings is rotated from the planar triazole rings with torsion angles ranging from -28.6(5)° (for N23-N13-C33-C83) to 6.9(5)° (for N21-N11-C31-C81) and 51.0(5)° (for N22-N12-C32-C82). The crystal shows normal W1-P1 (2.4829(10) Å) and P-C bond lengths (1.804(4)-1.810(4) Å).

Next, by blocking the phosphorus site with an oxide, we set out to explore the ligating ability of the three triazole groups of **6c**. Reaction with 1 equiv. of $RhCl_3 \cdot xH_2O$ in refluxing ethanol/THF resulted in an orange precipitate **9** (65% yield), soluble in DMF and DMSO, that shows a small upfield shift to $\delta(^{31}P)$ -9.5 ppm for the P=O group and deshielded triazole ring protons at $\delta(^{1}H)$ 10.0 ppm. Crystallization from DMF/EtOH afforded small orange needles suitable for a X-ray crystal structure analysis.

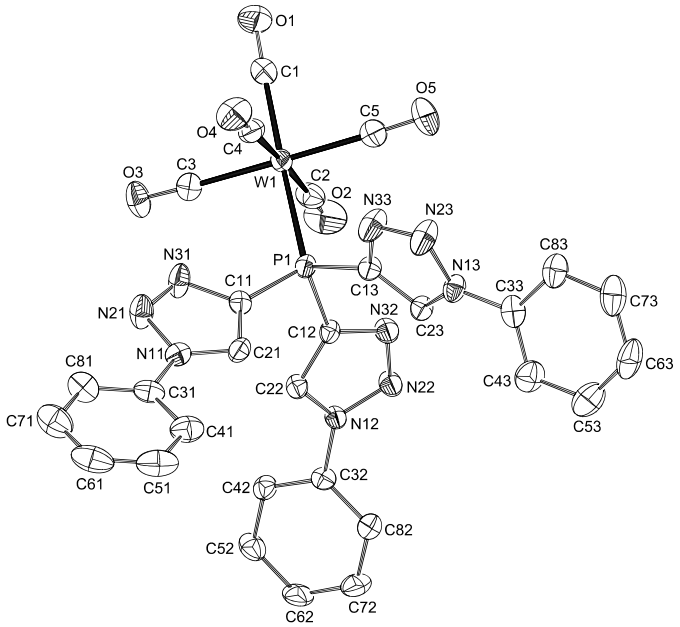
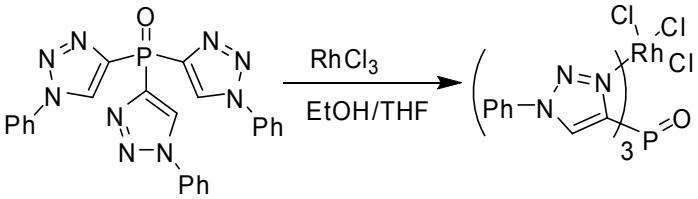


Figure 1 Displacement ellipsoid plot of **8** drawn at the 50% probability level. Hydrogen atoms and co-crystallized THF are omitted for clarity. Selected bond lengths [Å], angles and torsion angles [°]: W1-P1 2.4829(10), W1-C1 2.003(4), W1-C3 2.059(4), P1-C11 1.810(4), P1-C12 1.805(3), P1-C13 1.804(4), C1-O1 1.147(5), C3-O3 1.138(4), C11-C21 1.372(5), C11-N31 1.351(4), C21-N11 1.338(5), N11-N21 1.342(4), N21-N31 1.304(4), C31-N11 1.442(5), P1-W1-C1 174.79(12), P1-W1-C3 93.52(11), W1-P1-C11 115.80(12), C11-P1-C12 101.74(16), P1-C11-N31 120.7(3), N11-C21-C11 105.7(3), N21-N11-C21 109.9(3), N11-N21-N31 107.6(3), N21-N31-C11 109.5(3), N21-N11-C21-C11 -0.1(4), C21-N11-N21-N31 0.3(4), N21-N11-C31-C81 6.9(5), N22-N12-C32-C82 51.0(5), N23-N13-C33-C83 -28.6(5);



Scheme 7. Complexation of phosphine oxide **6c** to rhodium(III)chloride

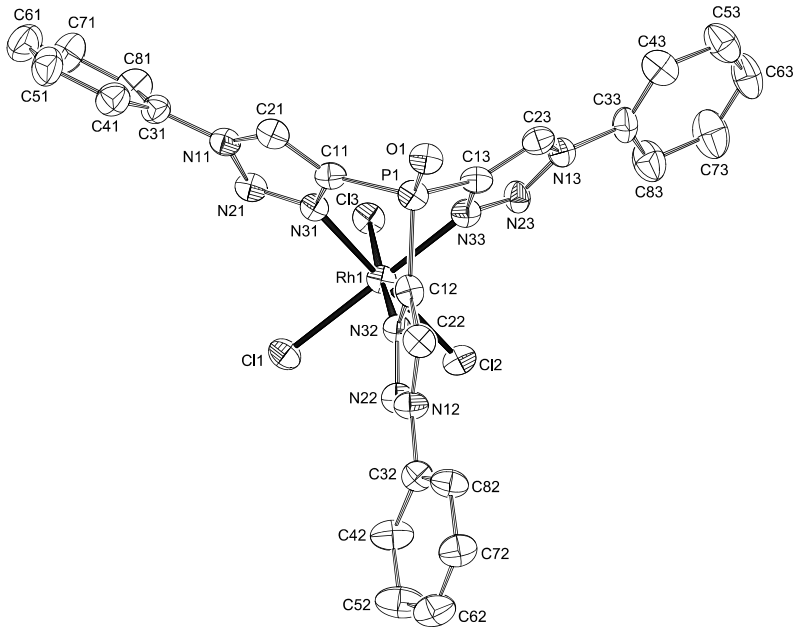
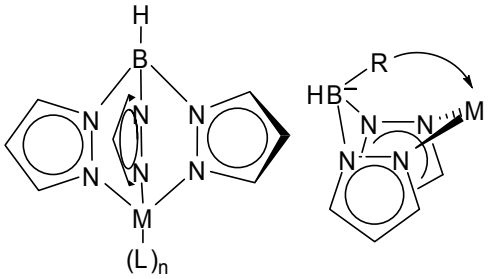


Figure 2 Displacement ellipsoid plot of **9** drawn at the 50% probability level. Hydrogen atoms and disordered solvent molecules are omitted for clarity. Selected bond lengths [Å], angles and torsion angles [°]: Rh1–Cl1 2.3187(12), Rh1–Cl2 2.3170(11), Rh1–Cl3 2.3081(12), Rh1–N31 2.057(4), Rh1–N32 2.062(4), Rh1–N33 2.044(4), P1–O1 1.463(3), P1–C11 1.781(5), P1–C12 1.784(5), P1–C13 1.796(5), N11–N21 1.352(5), N21–N31 1.308(5), N11–C21 1.354(6), N11–C31 1.435(6), N31–C11 1.369(6), C11–C21 1.364(6), Cl1–Rh1–Cl2 90.58(4), Cl1–Rh1–Cl3 92.55(4), Cl2–Rh1–Cl3 90.51(4), Cl1–Rh1–N31 90.65(11), Cl2–Rh2–N32 90.31(11), Cl3–Rh1–N33 88.27(11), N31–Rh1–N32 88.36(15), O1–P1–C11 116.8(2), C11–P1–C12 99.9(2), N11–C21–C11 105.9(4), N21–N11–C21 111.2(4) N21–N11–C31 120.1(4), N11–N21–N31 105.2(4), N21–N31–C11 111.8(4), Rh1–N31–N21 125.1(3), N31–C11–C21 106.0(4), Cl1–Rh1–N31–N21 –42.8(3), N11–N21–N31–Rh1 177.9(2), N31–N21–N11–C21 0.2(5), N21–N11–C31–C81 –37.7(6), N21–N11–C21–C11 –0.1(5), N31–C11–C21–N11 0.0(5), O1–P1–C11–C21 –1.9(5)

The molecular structure in the crystal of **9** is propeller shaped with the three phenyl groups rotated by –16.4(6)°, –18.2(6)°, and –37.7(6)° in the same direction from the planar triazole rings. The chloride and triazole groups are bisected. The P=O group and the transition metal are on the axle of the propeller (O1–P1–Rh1 179.42(14)°). $RhCl_3$ is coordinated to the 3-position of each of the triazole rings (Figure 2). The angles around Rh are close to the ideal 90° for an octahedron. The N=N double bonds of the

triazole rings (1.307(5)-1.310(5) Å) are slightly elongated and the N-N single bonds (1.352(5)-1.359(5) Å) correspondingly shortened, but they do not differ much from those of **8** (1.304(4)-1.317(4) Å and 1.351(4)-1.371(4) Å, respectively)



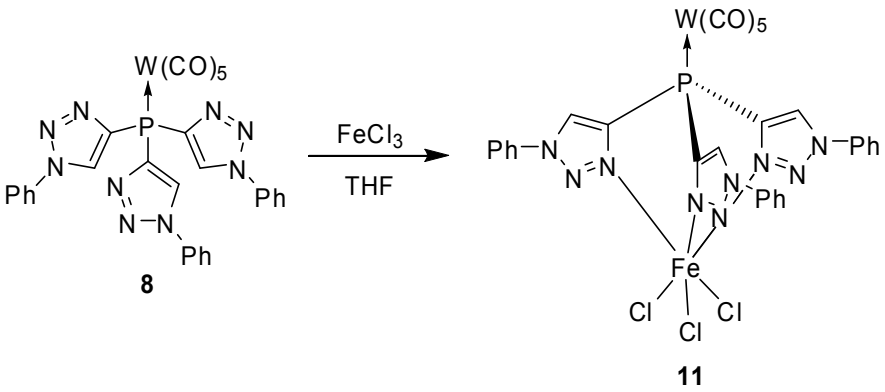
10

Structure **9** is remarkably similar to tris(pyrazolyl)borate (Tp) complex **10**, termed homoscorpionate by Trofimenko,[19] that has found broad applicability. The large anionic Tp is a reliable spectator ligand that provides more steric shielding to the metal center than the C_5H_5 (Cp) and $C_5(CH_3)_5$ (Cp*) ligands. These tripodal N-ligands are referred to as "scorpionate" ligands, because of their ability to interchange between bidentate and tridentate coordination. The third pyrazole ring of the Tp group can be viewed as being curled toward the metal center like a "scorpion tail". (Homo)scorpionates are catalysts for a plethora of reactions.[20]

Tolman et al.[21a,b] reported on tris(pyrazolyl)phosphine oxides (OP(pz*)) with differently substituted pyrazolyl groups (pz*) that are accessible only by lengthy syntheses, and on their ligating potential with Cu(I) and Zn(II)-complexes.[21b] A X-ray crystal structure of the Zn(II)-complex revealed a bidentate coordination of the N-donor ligands. A high catalytic efficiency and moderate enantioselectivity was reported for the cyclopropanation of styrene with diazo esters using Cu(I)-(OP(pz*))

complexes as catalysts. A related $Mo(CO)_3$ complex was reported by Joshi *et al.*[22]

Finally, we wondered whether tris(1,2,3-triazole)phosphane **7c** could be coordinated to two transition metal groups, one to the phosphorus center and one to the three triazole groups. Complex **8** already carries $W(CO)_5$ and appears ideally suited to explore the second transition metal coordination. However, reaction of **8** with $RhCl_3$ in refluxing EtOH/THF gave the same two products, identified by $\delta(^{31}P)$ -11.2 (d, $^1J(P,Rh)$ = 116.5 Hz) and -16.6 ppm (d, $^1J(P,Rh)$ = 125.5 Hz), as the reaction of **7c** with 0.33 equiv. of $RhCl_3$. Unfortunately, neither product could be fully characterized, but we presume that the $W(CO)_5$ group has dissociated from **8** and that incomplete coordination of $RhCl_3$ occurs. Reaction of **8** with anhydrous $FeCl_3$ at room temperature in THF was more successful as an orange powder precipitated out of solution in 48 hours. Like **9**, the product is only soluble in DMSO and DMF. Unfortunately, we were unable to obtain suitable crystals for an X-ray crystal structure analysis. However, the HR-MS analysis showed the presence of both the $W(CO)_5$ and Fe metal centers. Also the ^{31}P NMR chemical shift at δ −38.9 ppm, which is slightly shielded from that of **8** (−42.3, ($^1J(P,W)$ = 257.8 Hz)) shows the expected $^1J(P,W)$ coupling constant of 255.2 Hz, indicating that the $W(CO)_5$ group is retained. Consequently, we believe that bimetallic complex **11** has indeed been formed in a respectable isolated yield of 84%. Because of the broad interest in bimetallic systems, particularly with respect to the communication between the metallic centers,[23] we continue to explore the synthetic accessibility of related systems using the new tris(1,2,3-triazole)phosphine ligand **7c**.



Scheme 8. Synthesis of a bimetallic W/Fe (tris-triazole)-phosphine

5.4 Conclusions

Four phosphorus substituted acetylenes were synthesized via a novel and simple procedure. Using a Cu(I)-catalyzed 1,3-dipolar 'click'-reaction these acetylenes react with phenylazide to give the corresponding 1,2,3-triazoles. As expected, only the 1,4-substituted isomer is formed with isolated yields > 70%. The phosphine oxides can be reduced in excellent yields by reaction with $PhSiH_3$. The triazole substituted phosphanes and phosphine oxides can be used as versatile ligands in coordination to transition metal groups. The phosphanes give P-coordinated complexation as demonstrated by the $W(CO)_5$-complex **8**, whereas the phosphine oxide gives complexes in which the transition metal is coordinated to the N3-atoms of the three triazole rings, as shown for Rh-complex **9**. A bimetallic W/Fe complex was obtained from coordination of $FeCl_3$ to $W(CO)_5$-complex **8**.

5.5 Experimental

Phenylazide[24] and $W(CO)_5$(acetonitrile)[25] have been prepared according to literature procedures. All experiments were performed under an

atmosphere of dry nitrogen. Solvents were purified, dried, and degassed by standard techniques. NMR spectra were recorded (300K) on a Bruker Advance 250 spectrometer (^{31}P; 85% H_3PO_4) (^{1}H, ^{13}C, internally referenced to residual solvent resonances). High-resolution mass spectra (HR-MS) were recorded on a Finnigan Mat 900 (70 eV). Fast Atom Bombardment (FAB) mass spectrometry was carried out using a JEOL JMS SX/SX 102A four-sector mass spectrometer, coupled to a JEOL MS-MP9021D/UPD system program. Samples were loaded in a matrix solution (3-nitrobenzyl alcohol) on to a stainless steel probe and bombarded with Xenon atoms with an energy of 3KeV. During the high resolution FAB-MS measurements a resolving power of 10,000 (10% valley definition) was used. IR spectra were recorded on a Mattson 6030 Galaxy spectrophotometer. Melting points were measured on samples in unsealed capillaries and are uncorrected.

Synthesis of phosphinoyl-ethynes:

(Diphenylphosphinoyl)acetylene ***5a***

Chlorodiphenylphosphine oxide (8.28 g, 35 mmol) was dissolved in 50 mL THF. The solution was cooled to 0 °C and a solution of 35 mmol TMS-C≡C-MgBr (0.5 M in THF) was slowly added. The reaction mixture was stirred at 0 °C for 30 min. and 1 hr at room temperature. Evaporation of the solvent and filtration over silica gel gave $Ph_2P(O)$-C≡C-TMS (9.55 g, 91%) as a light brown solid. This was dissolved in 150 mL THF, 0.5 mL H_2O was added, and the reaction was cooled to -78 °C. TBAF on silica (500 mg,1-1.5 mmol fluoride per gram) was added. The reaction mixture was then slowly warmed to room temperature and quenched with 1 mL H_2O. Evaporation of the solvent and column chromatography (silica gel, ethyl acetate/hexane 1:1) gave 6.50 g (81%) of $Ph_2P(O)$-C≡C-H as a white solid.

The NMR data of $Ph_2P(O)$-C≡C-TMS are identical to those reported in ref [13a].

$Ph_2P(O)$-C≡C-H : m.p. 55-56 °C; ^{31}P NMR ($CDCl_3$) δ = 9.5 (s); ^{1}H NMR ($CDCl_3$) (identical to ref [13a]) δ = 3.32 (d, ^{3}J(H,P) = 9.7 Hz, 1H; ≡C-H), 7.46-7.54 (m, 6H; Ph), 7.80-7.89 (m, 4H; Ph); ^{13}C NMR ($CDCl_3$) (identical to ref [13a]) δ = 79.0 (d, ^{1}J(C,P) = 160.2 Hz; P-C≡), 95.8 (d, ^{2}J(C,P) = 27.7 Hz; P-C≡*C*), 128.9 (d, ^{3}J(C,P) = 13.6 Hz; *m*-Ph), 131.1 (d, ^{2}J(C,P) =11.3 Hz; *o*-Ph), 132.4 (d, ^{1}J(C,P) = 122.0 Hz; *i*-Ph), 132.8 (d, ^{4}J(C,P) = 3.0 Hz; *p*-Ph); HR-MS Calcd. for $C_{14}H_{11}OP$ 226.0548, Found 226.0541

(Diethynyl-phosphinoyl)benzene ***5b***

$PhP(O)Cl_2$ (2.61 g, 15 mmol) was dissolved in 50 mL THF and cooled to 0 °C. TMS-C≡C-MgBr (30 mmol, ~0.4 M in THF) was added dropwise after which the reaction mixture was allowed to warm to room temperature. The ^{31}P NMR spectrum showed the complete conversion to the product. The solvent was evaporated under reduced pressure and the dark brown oil was dissolved in 400 mL diethylether. The dark brown organic layer was extracted with H_2O (2 x 200 mL), dried with $MgSO_4$, and evaporated under reduced pressure. The crude product was then dissolved in 50 mL THF with 0.5 mL H_2O, cooled to 0 °C, and TBAF on silica (500 mg, 1-1.5 mol% fluoride per gram) was added. The reaction mixture was allowed to warm up to room temperature and stirred for another hour. Column chromatography (silica gel, ethyl acetate/hexane 1:1) yielded **5b** (1.42 g, 54% as a light pink/brownish solid.

M.p. 83-84 °C; ^{31}P NMR ($CDCl_3$) δ = -19.5 (s); ^{1}H NMR ($CDCl_3$) δ = 3.40 (d, ^{3}J(H,P) = 11.0 Hz, 2H; ≡C-H), 7.45-7.52 (m, 3H; Ar), 7.82-7.92 (m, 2H; Ar); ^{13}C NMR ($CDCl_3$) δ = 78.7 (d, ^{1}J(C,P) = 194.2 Hz; P-C≡), 93.9 (d, ^{2}J(C,P) = 35.9 Hz; ≡C-H), 129.4 (d, ^{2}J(C,P) = 15.3 Hz; *m*-Ph), 130.8 (d, ^{3}J(C,P) = 12.8 Hz; *o*-Ph), 131.4 (d, ^{1}J(C,P) = 142.6 Hz; *i*-Ph), 133.8 (d, ^{4}J(C,P) = 3.1 Hz; *p*-Ph); IR (CH_2Cl_2): ν = 3287 cm^{-1} (m) C-H, 2061 cm^{-1} (s) C≡C, 1207 cm^{-1} (s) P=O; HR-MS Calcd. for $C_{10}H_7OP$ 174.0234, Found 174.0225;

Tris(ethynyl)phosphine oxide ***5c***

A solution of $P(O)Cl_3$ (307 mg, 2.00 mmol) in 10 mL dry THF was cooled to 0 °C. A solution of freshly prepared TMS-C≡C-MgBr (~0.3 M in THF) from TMS-C≡CH and EtMgBr was added dropwise until ^{31}P NMR showed complete conversion of the starting material. The dark brown reaction mixture was allowed to warm up to room temperature and the solvent was evaporated under reduced pressure. H_2O (50 mL) was added and extraction with diethyl ether (2x50 mL) gave a dark brown oil which was purified with column chromatography (silica gel, ethyl acetate). The ^{31}P NMR spectrum showed the formation of several triethynylphosphine oxides resulting from partial desilylation. Dissolving the dark brown oil in THF/H_2O (20 mL/0.25mL) with TBAF on silica (250 mg, 1-1.5 mol% fluoride per gram) and stirring the solution for 1 hour resulted in complete desilylation. Column chromatography (silica gel, ethyl acetate) gave **5c** (133 mg, 55%) as a pale white solid, which had to be stored at -30 °C.

M.p. 111-112 °C; ^{31}P NMR (C_6D_6) δ = -56.8 (s); ^{1}H NMR (C_6D_6) δ = 2.15 (d, ^{3}J(H,P) = 12.3 Hz; ≡C-H); ^{13}C NMR (C_6D_6) δ = 78.8 (d, ^{1}J(C,P) = 228.5 Hz; P-C≡), 91.8 (d, ^{2}J(C,P) = 44.2 Hz; ≡C-H); IR (CH_2Cl_2): ν = 3280 cm^{-1} (m) C-H, 2068 cm^{-1} (s) C≡C, 1235 cm^{-1} (m) P=O; HR-MS Calcd. for C_6H_3OP 121.9922, Found 121.9916;

Diisopropylamino-diethynylphosphine oxide ***5d***

*(i*Pr)$_2$NP(O)Br$_2$ (950 mg, 3.1 mmol) was dissolved in 10 mL THF and cooled to 0 °C. After dropwise addition of approx 2 equivalents TMS-C≡C-MgBr (~0.4 M in THF), the reaction mixture was allowed to warm up to room temperature. The ^{31}P NMR spectrum showed complete conversion to the product. The solvent was evaporated under reduced pressure and the light brown oil dissolved in 400 mL diethylether. The organic layer was extracted with H_2O (2 x 200 mL), dried with $MgSO_4$, and evaporated under reduced pressure. The crude product was then dissolved in 50 mL THF/H_2O (100:1), cooled in an ice-water bath, and TBAF on silica (250 mg, 1-1.5 mol%

fluoride per gram) was added. The reaction mixture was allowed to warm up to room temperature and stirred for another hour. Column chromatography (silica gel, ethyl acetate/hexane 1:1) yielded **5d** (415 mg, 68%) as a light yellow solid.

M.p: 134-135 °C; ^{31}P NMR ($CDCl_3$) δ = -21.4 (s) ^{1}H NMR ($CDCl_3$) δ = 1.31 (d, ^{3}J(H,H) = 6.8 Hz, 12H; CH_3), 3.05 (d, ^{3}J(H,P) = 11.6 Hz, 2H; ≡C-H), 3.60-3.74 (m, 2H; N-CH); ^{13}C NMR ($CDCl_3$) δ = 22.5 (d, ^{3}J(C,P) = 2.1 Hz; CH_3), 46.9 (d, ^{2}J(C,P) = 6.9 Hz; N-CH), 81.1 (d, ^{1}J(C,P) = 224.7 Hz; P-C≡), 88.3 (d, ^{2}J(C,P) = 41.5 Hz; ≡CH); IR (CH_2Cl_2): ν = 3285 cm^{-1} (m) C-H, 2063 cm^{-1} (m) C≡C, 1238 cm^{-1} (m) P=O HR-MS Calcd. for $C_{10}H_{16}NOP$ 197.0970, Found 197.0969;

Triazole synthesis by reaction with phenylazide

*Synthesis of triazole **6a***

Ethynyldiphenylphosphine oxide **5a** (226 mg, 1.00 mmol) and phenylazide (119 mg, 1.00 mmol) were suspended in a 1:1 mixture of water and *tert*-butyl alcohol (4 mL). Sodium ascorbate (0.100 mmol, 100 μL of freshly prepared 1M solution in water) was added, followed by copper(II) sulfate pentahydrate (3 mg, 0.01 mmol) in 50 μL of water. The reaction mixture was stirred overnight during which time a light yellow solid precipitated. The reaction mixture was extracted with dichloromethane (2x10 mL), dried with $MgSO_4$, and purified by column chromatography (silica gel, ethyl acetate / hexane 1:1 followed by 1% ethanol in ethyl acetate). Evaporation of the solvents gave **6a** (248 mg, 72%) as a white solid.

M.p. 191-192 °C; ^{31}P NMR ($CDCl_3$) δ = 17.4 (s); ^{1}H NMR ($CDCl_3$) δ = 7.49-7.55 (m, 9H; *m*-Ph & *p*-Ph), 7.74 (d, ^{3}J(H,H) = 7.1 Hz, 2H; *o*-Ph on triazole ring), 7.90-7.99 (m, 4H; o-Ph on P), 8.63 (s, 1H; =C-H); ^{13}C NMR ($CDCl_3$) δ = 121.0 (s, *o*-Ph triazole), 128.8 (d, ^{3}J(C,P) = 12.8 Hz, *m*-Ph), 129.3 (d, ^{2}J(C,P) = 23.5 Hz; P-C=*C*H-N), 129.6 (s, *p*-Ph-N), 130.2 (s, *m*-Ph-N), 131.8 (d, ^{2}J(C,P) = 9.7 Hz, *o*-Ph), 132.5 (s, *p*-Ph), 132.5 (d, ^{1}J(C,P) = 110.5

Hz; *i*-Ph), 136.7 (s, *i*-Ph), 143.1 (d, ^{1}J(C,P) = 143.2 Hz; P-C-N); HR-MS FAB+, [M+H], Calcd. for $C_{20}H_{17}N_3OP$ 346.1109, found 346.1110

Triazole ***6b***

Diethynylphenylphosphine oxide **5b** (509 mg, 2.93 mmol) and phenylazide (700 mg, 5.88 mmol) were suspended in a 1:1 mixture of water and *tert*-butyl alcohol (12 mL). Sodium ascorbate (0.3 mmol, 0.3 mL of freshly prepared 1M solution in water) and $CuSO_4$ (15 mg, 0.06 mmol) in 100 μL of water were added. The reaction mixture was stirred overnight during which time a light yellow solid precipitated. Extraction with dichloromethane and column chromatography (silica gel, ethyl acetate / hexane 1:1 followed by 1% ethanol in ethyl acetate) resulted in the isolation of **6b** (890 mg, 74%) as a white solid.

M.p. 179-180 °C; ^{31}P NMR ($CDCl_3$) δ = 5.3 (s); ^{1}H NMR ($CDCl_3$) δ = 7.43-7.56 (m, 9H; *m*-Ph & *p*-Ph), 7.73 (d, ^{3}J(H,H) = 7.1 Hz, 4H; *o*-Ph on triazole ring), 8.10-8.19 (m, 2H; o-Ph on P), 8.57 (s, 2H; =C-H); ^{13}C NMR ($CDCl_3$) δ = 121.2 (s, *o*-Ph triazole), 129.0 (d, ^{2}J(C,P) = 26.5 Hz; P-C=*C*H-N), 129.0 (d, ^{3}J(C,P) = 13.4 Hz, *m*-Ph), 129.8 (s, *p*-Ph-N), 130.2 (s, *m*-Ph-N), 131.8 (d, ^{2}J(C,P) = 10.6 Hz, *o*-Ph), 133.1 (s, *p*-Ph), 136.6 (s, *i*-Ph triazole), 142.7 (d, ^{1}J(C,P) = 144.8 Hz; P-*C*-N); HR-MS FAB+, [M+H], calcd. for $C_{22}H_{18}N_6OP$ 413.1280, found 413.1280

Triazole ***6c***

Triethynylphosphine oxide **5c** (122 mg, 1.00 mmol) and phenylazide (357 mg, 3.00 mmol) were suspended in a 1:1 mixture of water and *tert*-butyl alcohol (4 mL). Sodium ascorbate (0.2 mmol, 200 μL of freshly prepared 1 M solution in water) was added, followed by copper(II) sulfate pentahydrate (6 mg, 0.02 mmol) in 50 μL of water. The reaction mixture was stirred overnight, during which time a brown solid precipitated. The reaction mixture was extracted with dichloromethane (2x10 mL), dried with $MgSO_4$, and purified by column chromatography (silica gel, ethyl acetate / hexane

1:1 followed by 1% ethanol in ethyl acetate). Evaporation of the solvents gave **6c** (350 mg, 73%) as a light yellow solid.

M.p. 201-202 °C; ^{31}P NMR ($CDCl_3$) δ = -5.7 (s); ^{1}H NMR ($CDCl_3$) δ = 7.48-7.58 (m, 9H; *m*-Ph & *p*-Ph), 7.77 (d, ^{3}J(H,H) = 6.9 Hz, 6H; *o*-Ph), 8.87 (s, 3H; =C-H); ^{13}C NMR ($CDCl_3$) δ = 121.3 (s, *o*-Ph), 129.8 (s, *p*-Ph), 129.8 (d, ^{2}J(C,P) = 28.6 Hz; P-C=*C*H-N), 130.2 (s, *m*-Ph), 136.5 (s, *i*-Ph), 141.2 (d, ^{1}J(C,P) = 157.1 Hz; P-*C*-N); HR-MS FAB+ [M+H], calcd. for $C_{24}H_{19}N_9OP$ 480.1450, found 480.1447

*Triazole **6d***

Diethynyldiisopropylaminophosphine oxide **5d** (600 mg, 3.07 mmol) and phenylazide (730 mg, 6.14 mmol) were suspended in a 1:1 mixture of water and *tert*-butyl alcohol (12 mL). Sodium ascorbate (0.6 mmol, 600 μL of freshly prepared 1 M solution in water) was added, followed by copper (II) sulfate pentahydrate (15 mg, 0.06 mmol) in 100 μL of water. The reaction mixture was stirred overnight, during which time a light brown solid precipitated. After filtration and column chromatography of the solid (silica gel, EtOAc/EtOH 95:5), **6d** (0.97 g, 72%) was isolated as a light yellow solid.

m.p. 231-232 °C, ^{31}P NMR ($CDCl_3$) δ = 7.8 (s); ^{1}H NMR ($CDCl_3$) δ = 1.34 (d, ^{3}J(H,H) = 6.7 Hz, 12H; CH_3), 3.69-3.82 (m, 2H; P-N-CH), 7.43-7.57 (m, 6H; *m*-Ph & *p*-Ph), 7.75-7.80 (m, 4H; *o*-Ph), 8.48 (s, 2H; P-C=C-H); ^{13}C NMR ($CDCl_3$) δ = 23.1 (d, ^{3}J(C,P) = 1.8 Hz; CH_3), 47.0 (d, ^{2}J(C,P) = 5.9 Hz; *C*H-CH_3), 121.0 (s, *o*-Ph), 128.3 (d, ^{2}J(C,P) = 28.6 Hz; P-C=*C*H-N), 129.5 (s, *p*-Ph), 130.2 (s, *m*-Ph), 136.8 (s, *i*-Ph), 144.9 (d, ^{1}J(C,P) = 167.9 Hz; P-*C*=); HR-MS FAB+ [M+H], Calcd. for $C_{22}H_{27}N_7OP$ 436.2015, found 436.2027

Reduction of 6a to 7a

A mixture of triazole **6a** (345 mg, 1.00 mmol) and $PhSiH_3$ (875 mg, 8.1 mmol) was heated at 100 °C for 12 hours. After evaporation of excess

$PhSiH_3$ at reduced pressure a white sticky solid remained, which was dissolved in diethyl ether and filtered over a short silica gel column. Diethyl ether was evaporated and the residue was extracted with hexane resulting in a white solid residue consisting of pure phosphine **7a**. (310 mg, 94%)
M.p. 119-120 °C; ^{31}P NMR ($CDCl_3$) δ = -32.4 (s); ^{1}H NMR ($CDCl_3$) δ = 7.34-7.68 (m, 13H; Ph), 7.68 (m, 2H; *o*-Ph on N), 7.81 (s, 1H; P-C=CH-N); ^{13}C NMR ($CDCl_3$) δ = 120.9 (s, *o*-Ph on N), 127.5 (d, ^{2}J(C,P) = 24.0 Hz; P-C=*C*H-N), 128.8 (d, ^{3}J(C,P) = 7.3 Hz, *m*-Ph), 129.0 (s, *p*-Ph-N), 129.4 (s, *m*-Ph-N), 130.0 (s, *p*-Ph), 133.9 (d, ^{2}J(C,P) = 20.0 Hz, *o*-Ph), 136.3 (d, ^{1}J(C,P) = 6.6 Hz; *i*-Ph on P), 137.1 (s, *i*-Ph on N), 145.9 (d, ^{1}J(C,P) = 6.7 Hz; P-*C*=CH-N); HR-MS FAB+ [M+H] Calcd for $C_{20}H_{17}N_3P$ 330.1160, Found 330.1163

Reduction of 6c to 7c

A mixture of triazole **6c** (500 mg, 1.04 mmol) and $PhSiH_3$ (875 mg, 8.1 mmol) was heated at 100 °C for 48 hours. Excess phenylsilane was evaporated leaving a sticky white solid. Filtration and washing with hexane yielded pure phosphine **7c** (430 mg, 90%) as an off-white powder. Slow oxidation in solution under air was observed.
M.p. 197-198°C (decomp.); ^{31}P NMR ($CDCl_3$) δ = -83.7 (s); ^{1}H NMR ($CDCl_3$) δ = 7.43-7.54 (m, 9H; Ph), 7.72-7.76 (m, 6H; *o*-Ph), 8.42 (s, 3H; P-C=CH-N); ^{13}C NMR ($CDCl_3$) δ = 121.0 (s, *o*-Ph), 128.1 (d, ^{2}J(C,P) = 23.5 Hz; P-C=*C*H-N), 129.3 (s, *p*-Ph), 130.1 (s, *m*-Ph), 137.0 (s, *i*-Ph), 142.7 (d, ^{1}J(C,P) = 4.5 Hz; P-*C*-N); HR-MS FAB+ [M+H] Calcd for $C_{24}H_{19}N_9P$ 464.1501, Found 464.1507

Synthesis of W-complex 8

Phosphine **7c** (690 mg, 1.49 mmol) was added to a solution of freshly prepared $W(CO)_5$[acetonitrile] (700 mg, 1.91 mmol) in 30 ml dry THF. The yellow solution was stirred overnight at room temperature. Evaporation of the solvent in vacuo yielded a dark yellow foam. Column chromatography

(silica gel, dichloromethane followed by hexane/ethyl acetate 1:1) yielded **8** (1.01 g, 86%) as a light yellow crystalline solid. Crystals were obtained from THF / Hexane at -20 °C.

M.p. 211-212 (decomp.); ^{31}P NMR ($CDCl_3$) δ = -42.3 (s, ^1J(P,W) = 257.8 Hz); ^{1}H NMR ($CDCl_3$) δ = 7.43-7.56 (m, 9H; *m*-Ph, *p*-Ph), 7.73-7.77 (m, 6H; *o*-Ph), 8.55 (s, 3H; P-C=CH-N); ^{13}C NMR ($CDCl_3$) δ = 121.1 (s, *o*-Ph), 127.6 (d, ^2J(C,P) = 24.0 Hz; P-C=*C*H-N), 129.8 (s, *p*-Ph), 130.2 (s, *m*-Ph), 136.7 (s, *i*-Ph), 142.8 (d, ^1J(C,P) = 73.7 Hz; P-*C*=CH), 196.4 (d, ^2J(C,P) = 7.1 Hz; CO_{eq}), 198.8 (d, ^2J(C,P) = 24.8 Hz; CO_{ax}); IR (CH_2Cl_2): ν(CO) = 2030 cm^{-1} (m), 1933 cm^{-1} (s), 1915 cm^{-1} (s); HR-MS FAB+ [M+H] Calcd for $C_{29}H_{19}N_9O_5PW$ 788.0756, Found 788.0776

Synthesis of Rh-complex 9:

Tris(phenyltriazole)phosphine oxide (280 mg, 0.58 mmol) was dissolved in 1 mL THF and diluted with 20 mL EtOH. $RhCl_3 \cdot xH_2O$ (135 mg, 0.6 mmol) was added and the reaction mixture was stirred under reflux for 3 hours. An orange solid precipitated immediately and was filtered off. The ^{31}P NMR spectrum showed complete conversion to a new product, which was only soluble in DMSO and DMF. Yield of **9**: 0.26 g, 65%

Crystals were obtained by slowly diffusing ethanol into a saturated solution of **9** in DMSO.

m.p 271-272 °C (decomp.) ^{31}P NMR (*d6*-DMSO) δ = -9.67 (s); ^{1}H NMR (*d6*-DMSO) δ = 7.56-7.71 (m, 9H; *m*-Ph & *p*-Ph), 7.90 (m, 6H; *o*-Ph), 10.0 (s, 3H; P-C=CH); ^{13}C NMR (d6-DMSO) δ = 121.4 (s, *o*-Ph), 130.1 (s, *m*-Ph), 130.6 (s, *p*-Ph), 131.1 (s, P-C=*C*), 135.4 (d, ^1J(C,P) = 149.8 Hz; P-C=), 135.5 (s, *i*-Ph); HR-MS FAB+, [MH], $C_{24}H_{19}N_9Cl_3OPRh$ calc. 687.9571, found 687.9565

Synthesis of $W(CO)_5$-$FeCl_3$-tristriazole complex 11

To a solution of $W(CO)_5$-complex **8** (40 mg, 0.050 mmol) in 0.5 mL THF was added a solution of anhydrous $FeCl_3$ (8.1 mg, 0.050 mmol) in 0.5 mL

THF. The color of the reaction mixture rapidly turned from yellow to orange. After stirring for 48 hours at room temperature, an orange solid had precipitated. Removal of the solution afforded **11** (40 mg, 84%) as an orange solid, soluble in DMSO and DMF.

M.p >185 °C (decomp.); ^{31}P NMR (*d6*-DMSO) δ = -38.9 (s, ^{1}J(P,W) = 255.2 Hz); ^{1}H NMR (*d6*-DMSO) δ = 7.30-7.80 (m, 9H; *m*-Ph, *p*-Ph), 7.83-8.35 (m, 6H; *o*-Ph), 9.17 (s, 3H; P-C=CH-N); ^{13}C NMR (*d6*-DMSO) δ = 119.3 (s, *o*-Ph), 126.8 (d, ^{2}J(C,P) = 17.1 Hz; P-C=*C*H-N), 128.0 (s, Ph), 128.6 (s, Ph), 134.8 (s, *i*-Ph), 140.0 (d, ^{1}J(C,P) = 78.2 Hz; P-*C*=CH), 194.8 (d, ^{2}J(C,P) = 7.6 Hz; CO_{ax}), 198.5 (d, ^{2}J(C,P) = 24.0 Hz; CO_{eq}); IR (KBr): ν(CO) = 2086 cm^{-1} (w), 2002 cm^{-1} (sh), 1953 cm^{-1} (vs); HR-MS FAB+ [M-2Cl] Calcd for $C_{29}H_{18}N_9O_5ClPFeW$ 877.9715, Found 877.9724

X-ray crystal structure determinations

X-ray intensities were measured on a Nonius Kappa CCD diffractometer with rotating anode (graphite monochromator, λ = 0.71073 Å). The structures were solved with automated Patterson methods[26] and refined with SHELXL-97[27] against F^2 of all reflections. Non hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were introduced in geometrically idealized positions and refined with a riding model. Geometry calculations and checking for higher symmetry was performed with the PLATON program[28].

Compound 8: $C_{29}H_{18}N_9O_5PW \cdot C_4H_8O$, Fw = 859.45, yellow needle, 0.18 x 0.09 x 0.06 mm^3, monoclinic, C2/c (no. 15), a = 27.6093(5), b = 20.4105(5), c = 13.53985(18) Å, β = 114.452(1)°, V = 6945.6(2) Å^3, Z = 8, D_x = 1.644 g/cm^3, μ = 3.43 mm^{-1}. 78673 Reflections were measured up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1} at a temperature of 150 K. An absorption correction based on multiple measured reflections was applied (0.56 - 0.81 correction range). 7986 reflections were unique (R_{int} = 0.0771). 451 parameters were refined with no restraints. R1/wR2 [I >

$2\sigma(I)$]: 0.0331/0.0576. R1/wR2 [all refl.]: 0.0623/0.0651. S = 1.031. Residual electron density between -0.89 and 1.08 e/Å^3.

Compound 9: $C_{24}H_{18}Cl_3N_9OPRh$ + disordered solvent, Fw = 688.70[*], yellow needle, 0.12 x 0.03 x 0.03 mm^3, monoclinic, $P2_1/c$ (no. 14), a = 9.3892(2), b = 16.7894(5), c = 21.7055(7) Å, β = 109.1762(10)°, V = 3231.78(16) Å^3, Z = 4, D_x = 1.415 g/cm^3[*], μ = 0.86 mm^{-1}[*]. 22074 Reflections were measured up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.53 Å^{-1} at a temperature of 125 K. An absorption correction was not considered necessary. 3940 reflections were unique (R_{int} = 0.0614). The crystal structure contains large voids (754.5 Å^3 / unit cell) filled with disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of the PLATON program[22] resulting in 197 electrons / unit cell. 352 parameters were refined with no restraints. R1/wR2 [$I > 2\sigma(I)$]: 0.0375/0.0899. R1/wR2 [all refl.]: 0.0529/0.0942. S = 1.013. Residual electron density between -0.55 and 0.60 e/Å^3.

[*] Derived values do not contain the contribution of the disordered solvent molecules.

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Chapter 6

Building Blocks for Phospha[*n*]pericyclynes

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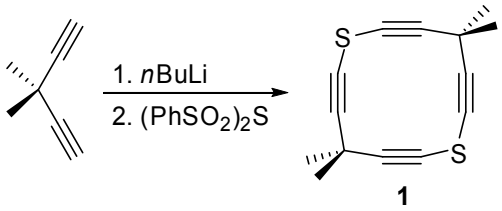
6.1 Abstract

Reaction of iPr$_2$NPCl$_2$ with acetylenic Grignard reagents resulted in the formation of new acetylenic substituted phosphorus building blocks. These building blocks can be protected by forming the corresponding W(CO)$_5$ complex and the =O and =S derivatives for added stability as was demonstrated for aminophosphine **11a**. From this building block, very sensitive product mixtures containing tetraphospha[4]pericyclynes **16** were obtained. In addition, the amino-substituent of phosphines **11** could be removed upon treatment with HCl to give chlorophosphine **18** from which novel trisethynylphosphines (**19**) bearing different substituted alkynes were obtained that may serve as building blocks for novel 3-dimensional phospha-acetylenic scaffolds such as the (di)ethynyl-expanded phosphacubanes **8** and **25** that, according to DFT calculations, have a higher degree of cyclic electron delocalization and reduced HOMO-LUMO gaps compared to their carbon-analogues.

6.2 Introduction

Acetylene-based carbon frameworks are important molecules both as target and as tool in advanced molecular architectures and materials.[1] In particular, the synthesis of macrocyclic oligoacetylenes, like the buta-1,3-diynediyl-expanded molecules, are being pursued for use in molecular recognition, as molecular switches, and in electro-optical devices.[2] In this report, we focus on a special class of acetylenic scaffolds, the phospha[*n*]pericyclynes. The term [*n*]pericyclyne, coined by Scott,[3] connotes a ring system of *n* acetylene functionalities with the numeral prefix [*n*] indicating the number of saturated corner units. The pericyclynes are with their rather simple and esthetically pleasing appearance a challenging and attractive research target from a synthetic[4] and theoretical[5] point of view. The incorporation of heteroatoms in such

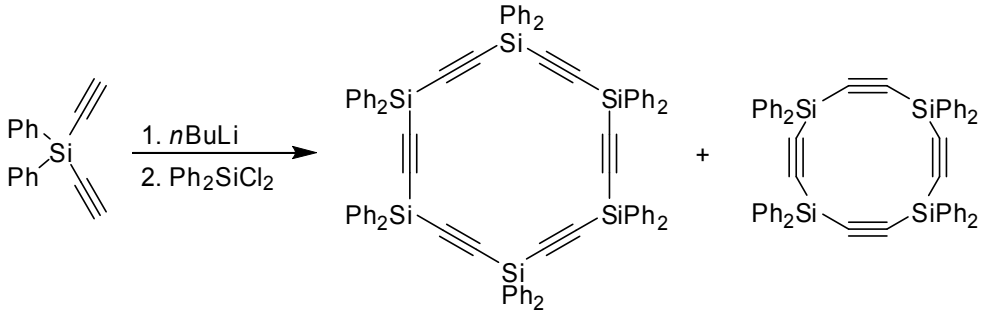
systems is still limited and has mainly focused on sulfur and silicon. Scott *et al*. reported the low yield (<15%) synthesis of dithia[4]pericyclyne **1** (Scheme 1) and related systems.[6] Attempts to synthesize tetrathia[4]pericyclynes have as of yet not succeeded.[7]



1

Scheme 1. Synthesis of dithia[4]pericyclyne **1**

Better accessible are the sila[*n*]pericyclynes (*n* = 3–6, 8, 10), bearing alkyl and aryl substituents, by treatment of double lithiated diethynylsilanes with dichlorosilanes (Scheme 2).[8] The ring structures with alternating R_2Si and C≡C units are planar and twisted in the solid state depending on their substituents and ring size.[8]

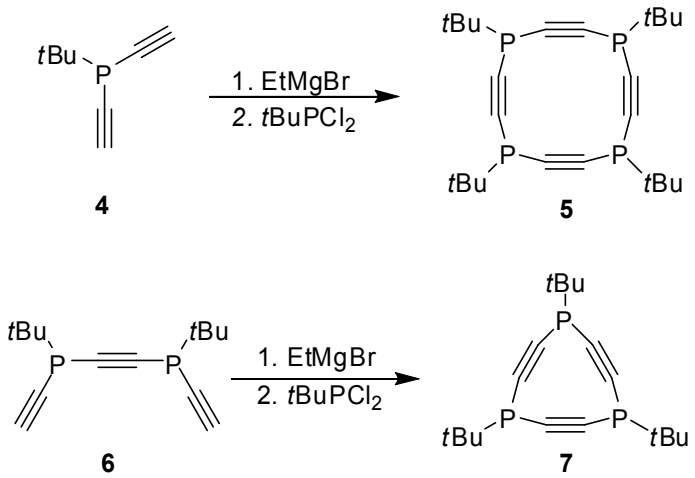


2 **3**

Scheme 2. Example of silapericyclyne synthesis

Few phosphorus containing pericyclynes are known, which is surprising considering the special P/C relationship.[9] In 1990, Scott *et al.*[10]

reported on the phospha-macrocycle **5** (11%; Scheme 3), obtained by double deprotonation of *tert*-butyldiethynylphosphine **4** using EtMgBr and subsequent reaction with *t*BuPCl$_2$. The smaller triphospha[3]pericyclyne **7** (16%) was obtained similarly from **6**.[6,10,11] A mixed P,Si-pericyclyne was synthesized by condensation of PhPCl$_2$ with Ph$_2$Si(C≡CH)$_2$ following the same stategy.[12] In 2000, Märkl *et al.*[13] reported on the so-called "exploded" phospha[*n*]pericyclynes (*n* = 3–6, 8) bearing butadiyne spacers instead of single acetylenes, which were synthesized in low yields by oxidative Eglington coupling of diethynylphosphine building blocks.

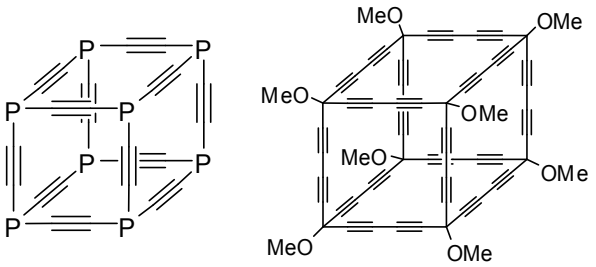


Scheme 3. Phosphapericyclyne synthesis

Typically, the acetylenic phosphine building blocks are synthesized by reacting chloro- or bromophosphines with metal acetylides, using Mg,[14a,b] Na,[14c] Li[14c] or Ti,[14d] as metal ion or with terminal alkynes using a Ni, Pd or Cu(I)-catalyzed coupling.[15]

So far the synthesis of hetero[*n*]pericyclynes has been limited to two-dimensional macrocycles, whereas the presence of phosphorus centers as corner units is ideally suited to construct cages like the ethynyl-expanded phosphacubane **8** (Scheme 4), in analogy to the diethynyl-expanded

cubane **9**.[16] The use of ethynylphosphines as building blocks has been briefly explored.[6] The synthesis of 3-dimensional phospha-acetylenic scaffolds would require a 'corner' molecule with either three differently protected acetylene groups, or two similar ones with an entirely different third protecting group that can be converted into an acetylenic unit after the (2-D) pericyclyne formation. Such phosphorus-based 'corner' molecules have to the best of our knowledge not yet been reported.



8 **9**

Scheme 4. (di)Ethynyl-expanded (phospha)cubanes

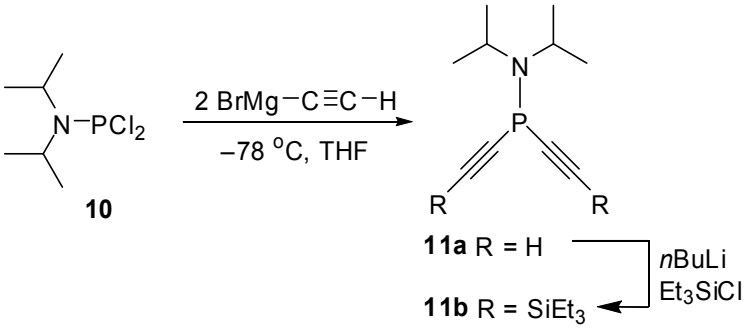
The focus of this paper is to explore the access to P-based building blocks for the construction of (exploded) phospha[*n*]pericyclynes. This report is an extension of recent work in which we examined the use of diethynylphosphine oxides toward 2-D pericyclyne formation.[17] In the present study the amine substituent is addressed for its suitability in the synthesis and its potential for further substitution/replacement toward 3-D structures.

6.3 Results and Discussion

A potential corner unit for the synthesis of phospha[*n*]pericyclynes is *P*,*P*-diethynyl-*N*,*N*-diisopropylphosphinous amide (**11a**) and we briefly address the stabilization of this building block by protection of its phosphorus lone-pair. From **11a**, tetraphospha[4]pericyclcynes are synthesized as highly sensitive product mixtures. Furthermore, we focus on the synthesis of triethynylphosphines[18] by substitution of the amine functionality in **11** to give novel building blocks for 3-dimensional structures. In the last section, we describe a brief computational analysis of (di-)ethynyl expanded phosphacubanes to investigate the properties of these unusual 3-D structures.

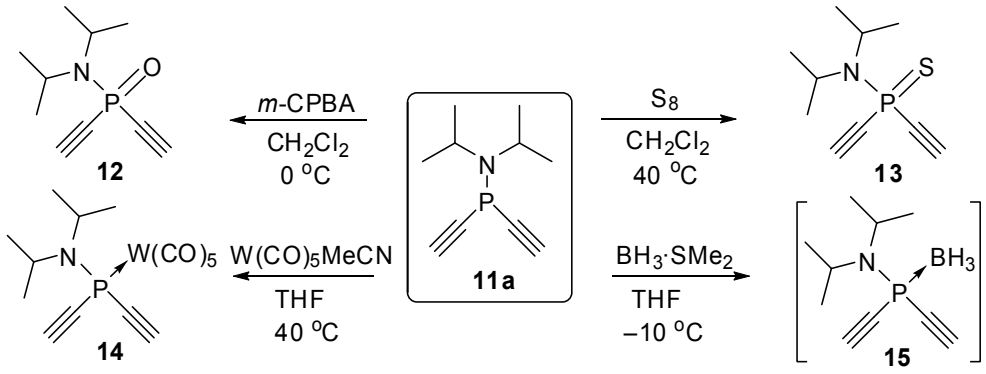
6.3.1 Corner Molecule

P,*P*-diethynyl-*N*,*N*-diisopropylphosphinous amide (**11a**) ($\delta(^{31}P)$ -14.9) was prepared from diisopropylphosphoramidous dichloride (**10**) ($\delta(^{31}P)$ +172.0) and HC≡CMgBr and isolated by distillation as an air-sensitive, colorless liquid (60%; Scheme 5), which was stable at -20 °C but decomposed quickly above 80 °C to give a tar-like black solid. Double lithiation of **11a**, using *n*-BuLi, and quenching with Et_3SiCl (TES-Cl) yielded the silyl-protected derivative **11b** ($\delta(^{31}P)$ -15.5; 94%).



Scheme 5. Synthesis of corner molecule **11**

The diethynylphosphines **11** are more stable as the corresponding P(V) species, which was established for the =O and =S derivatives and for the $W(CO)_5$ and BH_3 adducts (Scheme 6). Oxidation of **11a** with *m*-CPBA in CH_2Cl_2 yielded phosphine oxide **12** ($\delta(^{31}P)$ –21.4)[17] after chromatography as a white crystalline solid (65%) that is stable for months when stored at –30 °C. Stable sulfur analogue **13** was generated by reacting **11a** with S_8 in CH_2Cl_2 at 40 °C and isolated as yellow crystals (53%) after chromatography. Metal-complexation was effected by heating **11a** with $W(CO)_5[CH_3CN]$ in THF at 40 °C to obtain $W(CO)_5$-complex **14** ($\delta(^{31}P)$ –2.4, $^1J(P,W)$ = 286.5 Hz) in only 25% yield after chromatography due to decomposition of **11a** under the reaction conditions.[19] Protection of the phosphorus lone-pair with BH_3 can be attractive, because of the presumed ease of regenerating the phosphine.[20] Reaction of **11a** with $BH_3 \cdot SMe_2$ in THF at –10 °C gave indeed BH_3-adduct **15**, which is unfortunately not stable at room temperature as evidenced by the conversion of its $\delta(^{31}P)$ resonance at 19.0 ppm ($^1J(P,B)$ = 64 Hz) into two very broad resonances at 40 and 50 ppm. We believe that the second reaction concerns the hydroboration of the terminal alkynes in **15**.[21]



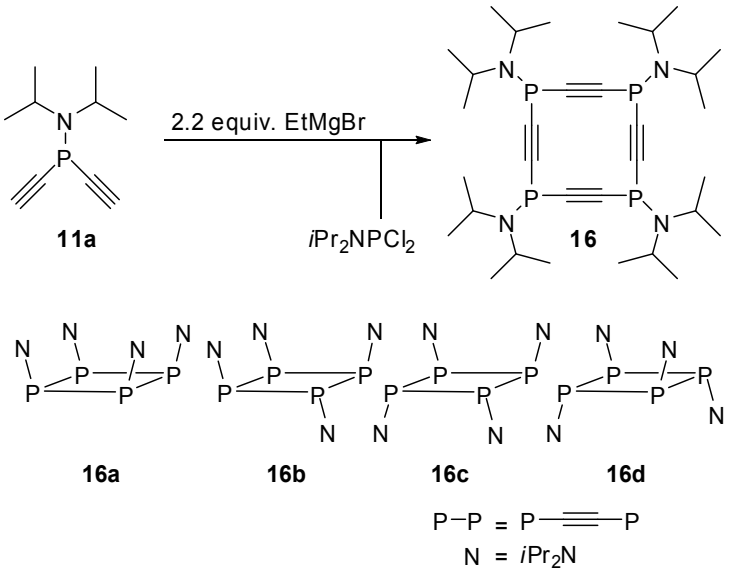
Scheme 6. Various protecting groups for P

Thus, the diethynyl(amino)phosphine building blocks can be stabilized by both derivatization and complexation. This aspect is relevant for manipulation of the phospha[*n*]pericyclyne products. However, the added stability intrinsically reduces the reactivity of the building blocks. For example, the oxide hampers the conversion of the amino-substituent into the third acetylene function,[17] and the sulfide was found sensitive toward reduction in the reaction of $P(S)Cl_3$ with acetylides.[22]

6.3.2 Pericyclyne Synthesis

The synthesis of amino-substituted phospha[4]pericyclyne **16** can be pursued via the so-called 'shotgun' approach[13,23] and in a stepwise manner by combining double deprotonated **11a** with dichloro(amino)phosphine **10**. In the 'shotgun' approach, the dianion of **11a**, obtained by reaction of **11a** with ethylmagnesium bromide in THF, was added slowly to a diluted solution of iPr$_2$NPCl$_2$ (**10**) in THF at –10 °C to give, after isolation and flash chromatography, a mixture of products as evidenced by the complex ^{31}P NMR that showed multiple resonances between –14 and –21 ppm (Figure 1). This is not surprising as, in analogy with the reported synthesis of the *t*Bu-derivative **5**, a mixture of four diastereomers can be expected (Scheme 7); the statistical ratio would be: **16a** (12.5%), **16b** (50%), **16c** (25%) and **16d** (12.5%) For symmetry reasons only single ^{31}P NMR resonances would be expected for each of the isomers **16a**, **c**, and **d**. Isolation of these isomers proved to be difficult, but their formation could be confirmed by their sharp singlet resonances at –17.8, –17.9 and –21.2 ppm in the ^{31}P NMR spectrum of the purified reaction mixture. The resonances at $\delta(^{31}P)$ –16.6 (t, ^3J(P,P) = 17.6 Hz; 1P), –18.6 (dd, ^3J(P,P) = 9.5 Hz, 17.6 Hz; 2P), and at –20.5 ppm (t, ^3J(P,P) = 9.5 Hz; 1P) are assigned to isomer **16b** and its P,P-coupling pattern confirms formation of the desired tetraphospha[4]pericyclyne. The ratio of the four stereoisomers was found to be 11:58:24:7, which is close to the theoretical values

(12.5:50:25:12.5) and the total yield of phospha[4]pericyclynes **16** is ca. 9% (Figure 1).



Scheme 7. One step 'shotgun' synthesis to tetraphospha[4]pericyclyne **16**

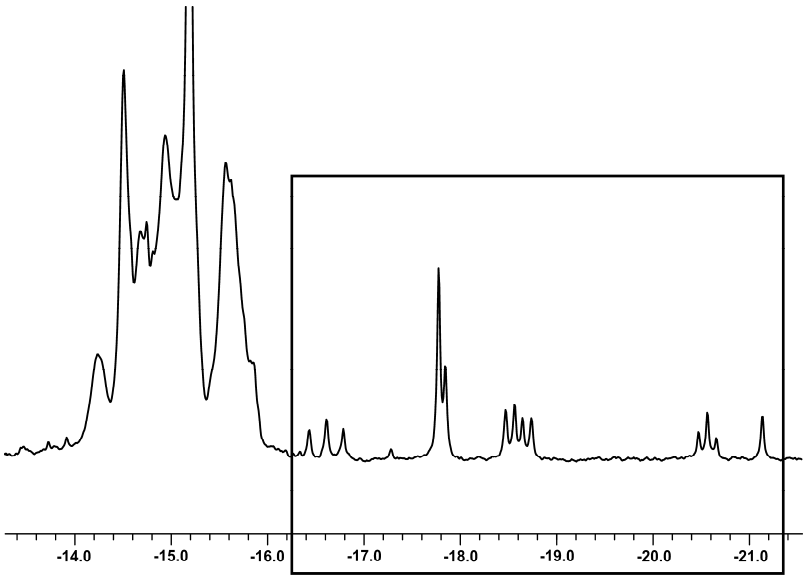
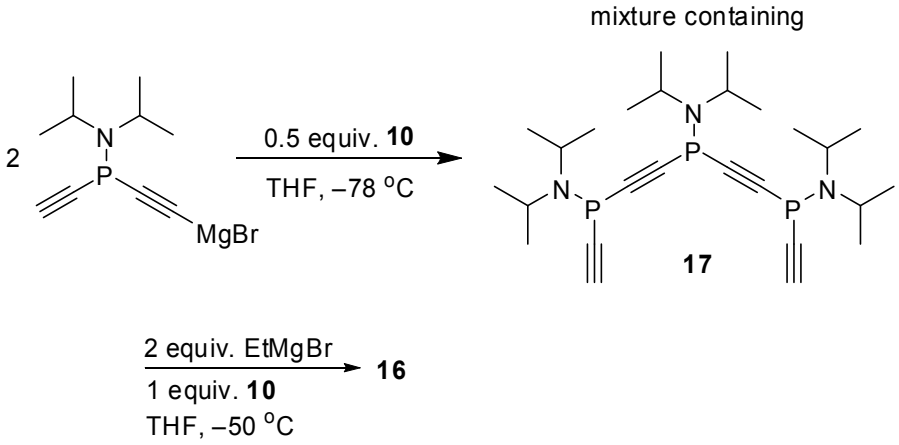


Figure 1. ^{31}P NMR spectrum reaction mixture containing phospha[4]pericyclyne **16**

The formation of **16** was confirmed by the parent mass ([M+H] 621.4) observed in the MS spectrum. Finally, we attribute the broad ^{31}P resonances that are observed in the range –14 to –16 ppm to differently sized oligomers. Due to the experimental conditions inherent to the 'shotgun' approach, the cyclic products have to compete with the favored formation of linear products.

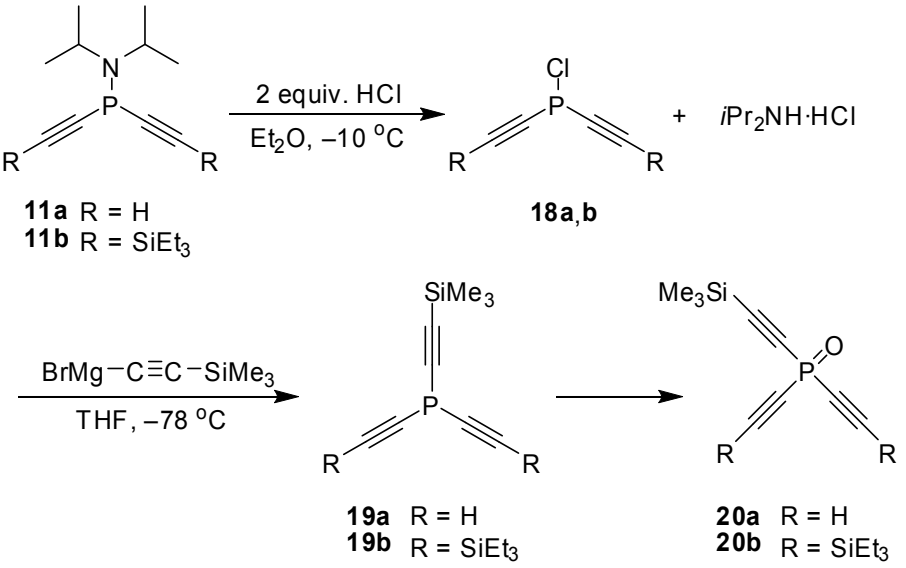
The stepwise approach to tetraphospha[4]pericyclyne **16** was pursued in the hope to limit the undesired formation of byproducts and to increase the yield and possibly the selectivity.[24] Thus, phosphine **11a** was deprotonated with 1 equiv. of EtMgBr and subsequently reacted with 0.5 equiv. of iPr$_2$NPCl$_2$ (**10**) to form triphosphine **17**, confirmed by MS ([M+H] m/z 492.2; Scheme 8). The product mixture was shown to be very sensitive toward oxygen and silica gel and therefore not further purified. Treatment of the crude reaction mixture with 2 equiv. of EtMgBr followed by slow addition to a dilute solution of iPr$_2$NPCl$_2$ (**10**) in THF resulted in the same mixture of products that was obtained by the 'shotgun' approach, be it with a slightly better ratio of **16a–d** to byproducts, according to ^{31}P NMR. Purification of macrocycle **16** was pursued by conversion to the corresponding sulfides but this led to complete decomposition.



Scheme 8. Stepwise synthesis toward tetraphospha[4]pericyclyne

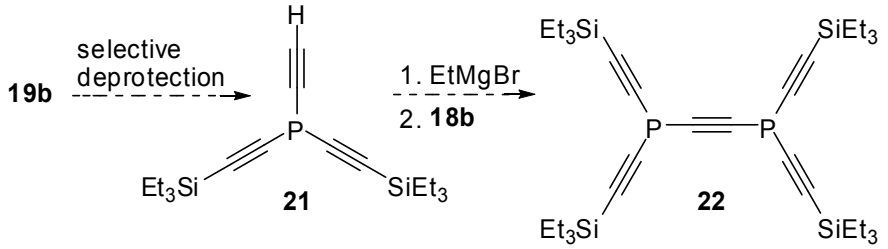
6.3.3 Amino Acetylene Exchange

Conversion of the amino-phospha[*n*]pericyclynes to e.g. triethynylphosphine building blocks is plausible, but only practical starting from the free phosphines. The potential of the amino-group on phosphorus to serve as a handle for further functionalization is known and reaction with HCl (g) leads to the formation of ammonium salts and chlorophosphines,[25] which we tested for model substrate **11**. Reaction of *i*Pr$_2$NP(C≡CH)$_2$ **11a** with HCl (0.1 M in Et$_2$O) in diethyl ether at -10 °C gave indeed immediate precipitation of *i*Pr$_2$NH·HCl and ^{31}P NMR spectroscopy confirmed the quantitative formation of the desired chlorophosphine **18** (δ(^{31}P) 18.5), which was moderately stable below 0 °C. For the related phosphine oxide **12**, this facile substitution of the amino-group does not occur.[17] Chlorophosphine **18** is an attractive building block for the synthesis of functionalized triethynylphosphines and we reacted **18** with BrMg-C≡CSiMe$_3$ to give phosphine **19a** (δ(^{31}P) -89.7) as the sole product (27%) after rapid filtration over silica gel. Its ^{31}P resonance is in close agreement to that of the C$_3$-symmetrical phosphines P-(C≡C-CH$_3$)$_3$ (δ(^{31}P) -87 ppm) and P-(C≡CH)$_3$ (δ(^{31}P) -91 ppm).[26] The volatile P(C≡CH)$_2$(C≡C-TMS) **19a** undergoes rapid oxidation by air, silica gel or other oxidants to yield the more stable phosphine oxide **20a** (δ(^{31}P) = -58.3 ppm). In analogy, silylated derivative **11b** (δ(^{31}P) -15.5) also showed clean conversion into the mixed triethynylphosphine **19b** (δ(^{31}P) -88.2), via chlorophosphine **18b** (δ(^{31}P) 16.1), and oxidation of **19b** by air to give **20b** (δ(^{31}P) -57.4).



Scheme 9. Synthesis of triethynylphosphines

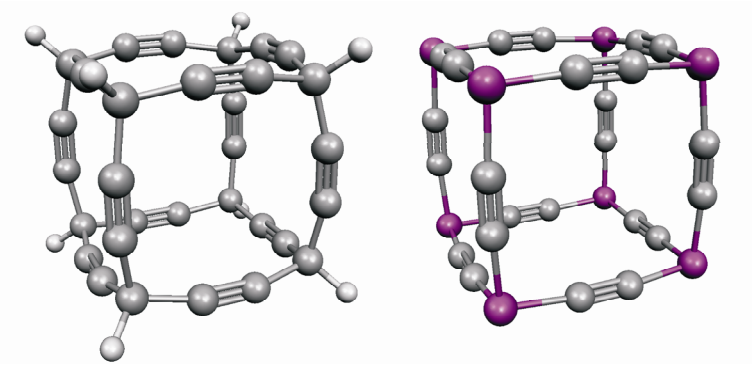
The triethynylphosphines **19**, bearing differently protected acetylenes, are promising building blocks for the selective synthesis of larger phosphap[*n*]pericyclynes, like bis(diethynylphosphino)ethyne **22** (Scheme 10) that can lead to 3-dimensional acetylenic phosphines, such as the ethynyl-expanded phosphacubane **8**.[27]



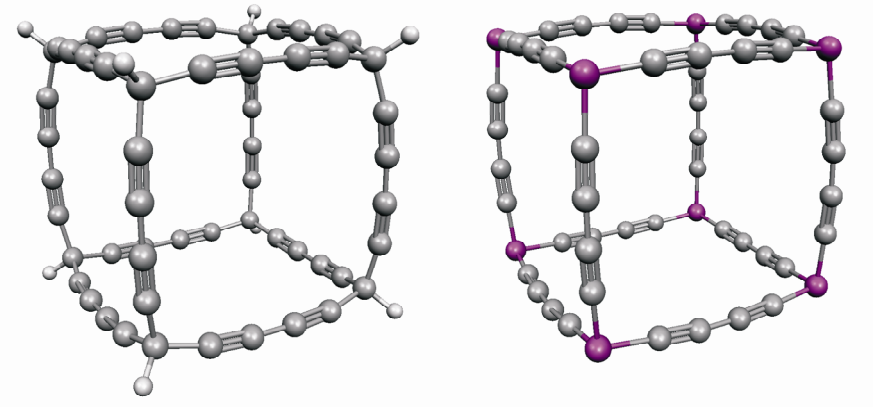
Scheme 10. Synthetic approach towards larger phospha[*n*]pericyclynes

To investigate the properties of these aesthetically pleasing molecules, we resorted to DFT calculations on phosphacubane **8**, its diethynyl-

expanded derivative **25**, and their carbon analogues **23** and **24** (Figure 2), of which **24**[28] is the parent structure of the octamethoxy-substituted cubane **9**.[16] Geometry optimizations (all *Oh* symmetry), performed at the B3PW91/6-31G(d) level of theory,[29] show that the phosphacubanes **8** and **25** enjoy a substantial degree of cyclic electron delocalization[6,28a] as their C≡C bonds are elongated (**23**: 1.208 vs. **8**: 1.218 and **24**: 1.215 vs. **25**: 1.222 Å) and their internal C–C bonds shortened (**24**: 1.363 vs. **25**: 1.359 Å) compared to their carbon analogues. In addition, phosphacubanes **8** and **25** show reduced HOMO–LUMO gaps, calculated at HF/6-311+G(2df,p)//B3PW91/6-31G(d),[29] compared to their C-analogues (**23**: 11.27 vs. **8**: 10.56 and **24**:[28a] 10.56 vs. **25**: 9.65 eV),[29] which makes the phosphacubanes interesting synthetic targets and therefore further studies on these remarkable phosphines (or their P(V) counterparts) and their (opto-electronic)properties are needed.



Ethynyl-expanded cubane **23**, ethynyl-expanded phosphacubane **8**



Diethynyl-expanded cubane **24**

diethynyl-expanded phospha-cubane **25**

Figure 2. Calculated structures of (di)ethynyl-expanded (phospha)cubane **8, 23-25** (all *Oh* symmetry) at the B3PW91/6-31G(d) level of theory. Selected bond lengths [Å] and angles [°]. Ethynyl-expanded cubane **23**: HC-C 1.480, C≡C 1.208; C-CH-C 107.0, HC-C≡C 166.6. Ethynyl-expanded phosphacubane **8**: P-C 1.783, C≡C 1.218; C-P-C 96.6, P-C≡C 175.2. Diethynyl-expanded cubane **24**: HC-C 1.475, C≡C 1.215, C-C 1.363; C-CH-C 108.5, HC-C≡C 169.4, C≡C-C 175.7. Diethynyl-expanded phosphacubane **25**: P-C 1.770, C≡C 1.222, C-C 1.359; C-P-C 98.5, P-C≡C 178.8, C≡C-C 174.9.

6.4 Conclusions

Several building blocks for phospha[*n*]pericyclynes were synthesized. Phosphine **11a** is readily available from simple starting materials and its sensitivity can be controlled by $W(CO)_5$ complexation or conversion to the =O and =S derivatives. The formation of tetraphospha[4]pericyclynes **16** from **11a** is demonstrated, but their sensitivity towards oxidation hampers their isolation and further use. Chlorophosphines **18**, obtained from phosphines **11** and HCl, gives access to triethynylphosphines **19** with

various substituents on the acetylene. With these molecules now accessible, we believe the synthesis of 3-dimensional structures such as the ethynyl-expanded phosphacubanes **8** and **25** is one step closer. According to DFT calculations, these aesthetically pleasing phosphacubanes have, when compared to their carbon-analogues, a higher degree of cyclic electron delocalization and reduced HOMO-LUMO gaps.

6.5 Experimental

Computations. Geometry optimizations (B3PW91/6-31G(d)) and single-point energy computations (HF/6-311+G(2df,p)//B3PW91/6-31G(d)) were carried out with density functional theory (DFT) using the Gaussian03 suite of programs.[29] Vibrational analyses were performed at the B3PW91/6-31G(d) level of theory to verify whether minima were obtained on the potential energy surface.

General. BrMg-C≡C-$SiMe_3$,[30] BrMg-C≡C-H[30] and iPr_2NPCl_2 (**10**)[31] were prepared according to literature procedures. All experiments were performed under an atmosphere of dry nitrogen. Solvents were purified, dried, and degassed by standard techniques. ^1H, ^{13}C and ^{31}P NMR spectra were recorded at 300 K on Bruker Avance 250 (respectively 250.13, 62.90 and 101.25 MHz) or MSL 400 (respectively 400.13, 100.64 and 162.06 MHz) spectrometers. ^1H and ^{13}C NMR spectra were internally referenced to residual solvent resonances and ^{31}P NMR spectra externally to 85% H_3PO_4. Low Resolution Mass Spectroscopy was performed by direct infusion analysis of a methanol solution containing the phosphine into an ion trap mass spectrometer (LCQ-deca, Thermo Electron). High-resolution mass spectra (HRMS) were recorded on a Finnigan Mat 900 (EI, 70 eV). IR spectra were recorded on a Mattson 6030 Galaxy spectrophotometer. Melting points were measured on samples in unsealed capillaries and are uncorrected.

iPr$_2$N-P[C≡CH]$_2$ ***11a***. A solution of freshly prepared HC≡C-MgBr (ca. 0.5M in THF) was added to a solution of *i*Pr$_2$N-PCl$_2$ (11.9 g, 58.9 mmol) in THF (100 mL) at -78 °C. The reaction was monitored by ^{31}P NMR to stop the addition of the Grignard reagent (120 mL added) after complete conversion of *i*Pr$_2$NPCl$_2$ was observed. After quenching of the reaction mixture with a few drops of water, solvent evaporation under reduced pressure, and extraction with diethyl ether (2 × 100 mL), a brown solid remained. Distillation at 60 °C/7 mmHg yielded **11a** as a colorless liquid (6.48 g, 60%), which solidified upon cooling and that can be stored at -20 °C for months without any signs of decomposition. Storage at room temperature caused a color change to brown. ^{31}P NMR ($CDCl_3$) δ = -14.9 (s); ^{13}C NMR ($CDCl_3$) δ = 23.4 (d, ^3J(C,P) = 7.6 Hz; CH_3), 49.7 (d, ^2J(C,P) = 8.9 Hz; N-CH), 83.8 (d, ^1J(C,P) = 10.9 Hz; P-C≡), 91.3 (d, ^2J(C,P) = 6.6 Hz; ≡CH); ^{1}H NMR ($CDCl_3$) δ = 1.15 (d, ^3J(H,H) = 6.7 Hz, 12H; CH_3), 2.98 (d, ^3J(H,P) = 1.4 Hz, 2H; ≡C-H), 3.60 (sp, ^3J(H,H) = 6.7 Hz, 2H; N-CH).

iPr$_2$NP(C≡C-TES)$_2$ ***11b***. n-BuLi (18.8 mmol, 1.6 M in hexanes) was added dropwise to a solution of phosphine **11a** (1.70 g, 9.4 mmol) in THF (200 mL) at -78 °C. The resulting solution was stirred for 3 h and quenched with freshly distilled Et_3SiCl (TES-Cl; 2.83 g, 18.8 mmol). The light yellow solution was evaporated under reduced pressure to yield a yellow oil that was filtered over Al_2O_3 with hexane to yield **11b** (3.61 g, 94%) as a light yellow oil. ^{31}P NMR ($CDCl_3$) δ = -15.5 (s); ^{13}C NMR ($CDCl_3$) δ = 4.5 (d, ^4J(C,P) = 6.8 Hz; $SiCH_2$), 7.5 (d, ^5J(C,P) = 2.6 Hz; $SiCH_2CH_3$), 23.3 (d, ^3J(C,P) = 7.5 Hz; $CH(CH_3)_2$), 49.4 (s, CH), 107.5 (d, ^1J(C,P) = 39.7 Hz; P-C≡), 112.7 (s, ≡C-Si); ^{1}H NMR ($CDCl_3$) δ = 0.61 (q, ^3J(H,H) = 7.8 Hz, 12H; $SiCH_2$), 1.00 (t, ^3J(H,H) = 7.8 Hz, 18H; $SiCH_2CH_3$), 1.16 (d, ^3J(H,H) = 6.8 Hz, 12H; $CH(CH_3)_2$), 3.65 (sp, ^3J(H,H) = 6.8 Hz, 2H; CH).

iPr$_2$*N–P(O)[C≡CH]*$_2$ **12.** A solution of dried *m*–CPBA in CH_2Cl_2 (2.0 mL, ~1 M) was added dropwise to a solution of phosphine **11a** (181 mg, 1.0 mmol) in CH_2Cl_2 (5 mL) at 0 °C and the reaction mixture was stirred at 0 °C for 1 h. ^{31}P NMR indicated a clean conversion to phosphine oxide **12**. The CH_2Cl_2 solution was washed with H_2O (2 × 5 mL), dried over $MgSO_4$, and purified by column chromatography (silica gel, ethyl acetate/hexane 1:3) to yield **12** (130 mg, 65%) as a pale white solid. M.p: 134–135 °C; ^{31}P NMR ($CDCl_3$) δ = –21.4 (s); ^{13}C NMR ($CDCl_3$) δ = 22.5 (d, ^3J(C,P) = 2.1 Hz; CH_3), 46.9 (d, ^2J(C,P) = 6.9 Hz; NCH), 81.1 (d, ^1J(C,P) = 224.7 Hz; PC≡), 88.3 (d, ^2J(C,P) = 41.5 Hz; ≡CH); ^{1}H NMR ($CDCl_3$) δ = 1.31 (d, ^3J(H,H) = 6.8 Hz, 12H; CH_3), 3.05 (d, ^3J(H,P) = 11.6 Hz, 2H; ≡CH), 3.60–3.74 (m, ^3J(H,P) = 21.2 Hz, ^3J(H,H) = 6.8 Hz, 2H; NCH); MS (70 eV): m/z (%): 197.1 (8) $[M]^+$, 182.1 (70) $[M - CH_3]^+$, 140.0 (100) $[M - NCH(CH_3)_2]^+$; HRMS: Calcd. for $C_{10}H_{16}NOP$ 197.0970, Found 197.09719.

iPr$_2$*N–P(S)[C≡CH]*$_2$ **13.** A solution of phosphine **11a** (680 mg, 3.75 mmol) and S_8 (721 mg, 2.81 mmol) in dichloromethane (40 mL) was heated at reflux for 24 h during which the solution slowly turned black. The solution was filtered and evaporation of dichloromethane at reduced pressure followed by column chromatography (silica gel, DCM/pentane 1:1) gave **13** (410 mg, 53%) as a yellow solid. M.p. 99–100 °C; ^{31}P NMR ($CDCl_3$) δ = 0.3 (s); ^{13}C NMR ($CDCl_3$) δ = 22.7 (d, ^3J(C,P) = 2.7 Hz; CH_3), 48.7 (d, ^2J(C,P) = 6.1 Hz; NCH), 81.7 (d, ^1J(C,P) = 192.4 Hz; PC≡), 88.9 (d, ^2J(C,P) = 36.1 Hz; ≡CH); ^{1}H NMR ($CDCl_3$) δ = 1.37 (d, ^3J(H,H) = 6.9 Hz, 12H; CH_3), 3.24 (d, ^3J(H,P) = 11.4 Hz, 2H; ≡CH), 3.84–3.99 (m, ^3J(H,P) = 21.2 Hz, ^3J(H,H) = 6.9 Hz, 2H; NCH); MS (70 eV): m/z (%): 213.1 (6) $[M]^+$, 198.1 (8) $[M - CH_3]^+$, 180.1 (50) $[M - HS]^+$, 156.0 (16) $[M - CH(CH_3)_2 - CH_3]^+$; HRMS: Calcd for $C_{10}H_{16}NPS$ 213.0741, Found 213.07466.

iPr$_2$*N–P[W(CO)*$_5$*][C≡CH]*$_2$ **14.** To a solution of phosphine **11a** (1.25 g, 6.90 mmol) in dry THF (10 mL) was added at once $W(CO)_5$[MeCN] (2.52 g, 6.90

mmol) and the reaction mixture was heated at 50 °C for 8 h. The resulting black solution was concentrated under reduced pressure and the residue was purified by column chromatography (silica gel, pentane/dichloromethane 4:1) to yield **14** (870 mg, 25%) as colorless crystals. M.p. 80–81 °C; ^{31}P NMR ($CDCl_3$) δ = –2.4 (s, ^1J(P,W) = 286.5 Hz); ^{13}C NMR ($CDCl_3$) δ = 23.2 (d, ^3J(C,P) = 4.8 Hz; CH_3), 52.1 (d, ^2J(C,P) = 9.5 Hz; NCH), 83.3 (d, ^1J(C,P) = 83.0 Hz; PC≡), 93.1 (d, ^2J(C,P) = 18.1 Hz; ≡CH), 196.9 (d, ^2J(C,P) = 8.2 Hz, ^1J(C,W) = 127.3 Hz; *cis*–CO), 199.7 (d, ^2J(C,P) = 26.7 Hz; *trans*–CO); ^{1}H NMR ($CDCl_3$) δ = 1.38 (d, ^3J(H,H) = 6.9 Hz, 12H; CH_3), 3.42 (d, ^3J(H,P) = 6.4 Hz, 2H; ≡CH), 3.92–4.10 (m, ^3J(H,H) = 6.9 Hz, 2H; NCH); IR (CH_2Cl_2) ν(CO) = 2077 (w, CO_{ax}), 1945 (vs, CO_{eq}) cm^{-1}; MS (70 eV): m/z (%): 505.1 (26) $[M]^+$, 449.1 (24) $[M-2CO]^+$, 421.1 (14) $[M-3CO]^+$, 365.1 (87) $[M-5CO]^+$; HRMS: Calcd for $C_{15}H_{16}NO_5P^{186}W$ 507.0309, Found 507.02640; Calcd for [M –2CO] 449.0378, Found 449.03696.

Reaction of iPr$_2$N–P[C≡CH]$_2$ ***11a*** *with BH$_3$·SMe$_2$*. To a cooled solution of phosphine **11a** (320 mg, 1.75 mmol) in THF (25 mL) was dropwise added $BH_3 \cdot SMe_2$ (1.0 mL, 2.0 mmol; 2 M in THF) at 0 °C. After 30 min at 0 °C, the ^{31}P NMR spectrum showed complete conversion of the starting material and a broad resonance appeared at δ = 19.0 ppm (^1J(P,B) = 64 Hz), indicating the formation of iPr$_2$N–P(BH$_3$)[C≡CH]$_2$ (**15**). Upon warming to room temperature, the reaction mixture slowly turned from yellow to orange and the signal at δ(^{31}P) 19.0 converted into very broad resonances at δ^{31}P 40 and 50 ppm that we presume to be polymeric material. The desired borane-adduct iPr$_2$N–P(BH$_3$)[C≡CH]$_2$ **15** could not be isolated.

Phosphapericyclynes ***16***. *A. Shotgun Synthesis*: Freshly prepared EtMgBr in THF (9 mL, ca. 1.0M) was added to a solution of **11a** (740 mg, 4.1 mmol) in THF (150 mL) at –50 °C. The resulting light brown, cloudy solution was stirred for 30 min., warmed to room temperature, and added slowly to a diluted (~0.03M) solution of iPr$_2$NPCl$_2$ (**10**) (909 mg, 4.5 mmol) in THF at –

10 °C, after which the black reaction mixture was stirred at room temperature for an additional 2 h. After removal of the solvent and multiple extractions with hexane, the dark brown oily product mixture was subjected to flash chromatography (silica gel, hexane) during which extensive product decomposition occurred. Low Resolution Mass Spectroscopy and ^{31}P NMR indicated the presence of the desired phospha[4]pericyclyne **16**. The product mixture was kept at –20 °C to prevent further decomposition. ^{31}P NMR ($CDCl_3$) δ = –17.8, –17.9 and –21.2 (**16a**,**c**,**d**); **16b**: ^{31}P NMR ($CDCl_3$) δ = –20.5 (t, ^3J(P,P) = 9.5 Hz), –18.6 (dd, ^3J(P,P) = 9.5 Hz, ^3J(P,P) = 17.6 Hz), –16.6 (t, ^3J(P,P) = 17.6 Hz); Low resolution mass spectroscopy of mixture: m/z 621.4 (M+H).

*B. Stepwise Synthesis via **17***: To a solution of **11a** (3.0 g, 16.6 mmol) in THF (300 mL) was added dropwise freshly prepared EtMgBr (85 mL, 0.2 M in THF, 1.1 equiv.) at –50 °C. After warming up to room temperature, this reaction mixture was slowly added together with a solution of **10** (1.67 g, 8.3 mmol) in THF (300 mL) to 200 mL of THF at –50 °C and stirred for and additional 1 h. After evaporation of the solvent at room temperature under reduced pressure the dark brown residue was extracted with hexane, filtered and kept at –70 °C to prevent product decomposition. ^{31}P NMR ($CDCl_3$) δ = –15.4 to –14.2 (multiple resonances); Low resolution mass spectroscopy of mixture: m/z 492.2 (M+H).

*Ring closure of **17** to **16***: To the hexane solution of triphosphine **17** at –50 °C was added 300 mL THF and then slowly a freshly prepared solution of EtMgBr (2 equiv. based on first step, 85 mL, 0.2 M). The resulting di-anion solution of **17** and a THF solution (300 mL) of **10** (1.67 g, 8.3 mmol) were simultaneously added in a dropwise manner to 200 mL of THF cooled to –50 °C. The product mixture containing **16** was obtained after solvent removal and extraction of the residue with hexane. The NMR spectroscopic data are similar to those obtained from the shotgun approach.

P(C≡CH)$_2$(C≡C-TMS) ***19a****:* A solution of phosphine **11a** (543 mg, 3.00 mmol) in diethyl ether (10 mL) was cooled in an ice-salt bath at -10 °C. To this solution was added a freshly prepared solution of HCl (~0.1 M) in diethyl ether. The reaction was followed by ^{31}P NMR and addition of HCl/Et$_2$O was stopped (31 mL added) when full conversion of **11a** to chlorophosphine **18a** (δ^{31}P 18.5) was observed. Filtration of the salts yielded a clear colorless solution. The etheral solution was concentrated to about 10% of its initial volume, while keeping the temperature below 0 °C. THF (10 mL) was added and the colorless solution was cooled to -78 °C. Subsequently, a freshly prepared solution of BrMg-C≡C-TMS (6 mL, 0.5M in THF) was added dropwise and the reaction mixture was slowly warmed up to room temperature. The solvent was evaporated under reduced pressure. The product was extracted with diethyl ether and the magnesium salts were washed with diethyl ether. The solution was filtered and evaporated and the remaining oil was purified by fast filtration (silica gel, hexane) to yield **19a** as a colorless oil (140 mg, 27%). Phosphine **19a** is highly sensitive and quickly oxidizes in air to the corresponding oxide **20a** (δ^{31}P -58.3). **19a**: ^{31}P NMR ($CDCl_3$) δ = -89.7 (s); ^{13}C NMR ($CDCl_3$) δ = -0.5 (s, CH_3), 75.3 (d, ^1J(C,P) = 1.4 Hz; P-C≡CH), 94.1 (s, P-C≡C-Si), 94.6 (d, ^2J(C,P) = 9.1 Hz; ≡CH), 116.8 (d, ^2J(C,P) = 2.1 Hz; ≡C-Si); ^{1}H NMR ($CDCl_3$) δ = 0.21 (s, 9H; CH_3), 3.09 (s, 2H; ≡CH).

P(C≡C-TES)$_2$(C≡C-TMS) ***19b****:* Phosphine **11b** (0.1 mmol) was reacted with HCl(g)/Et$_2$O and BrMg-C≡C-TMS to give trisethynylphosphine **19b** in analogy to the procedure described above for **19a**. The reaction was followed by ^{31}P NMR and showed that chlorophosphine **18b** (δ^{31}P 16.1) is cleanly converted to **19b**. Rapid filtration over silica gel resulted in partial conversion to the phosphine oxide **20b** (δ^{31}P (hexane) -57.4). Filtration of the mixture (**19b** and **20b**) over Al_2O_3 enabled the isolation of **19b**. ^{31}P NMR ($CDCl_3$) δ = -88.5 (s); ^{1}H NMR ($CDCl_3$) δ = 0.2 (s, 9H; $Si(CH_3)_3$), 0.64 (q, ^3J(H,H) = 7.8 Hz; $SiCH_2CH_3$), 1.02 (t, ^3J(H,H) = 7.8 Hz; $SiCH_2CH_3$).

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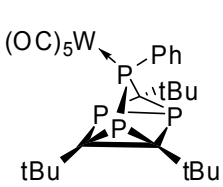
Samenvatting

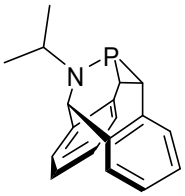
nieuwe cyclische organofosfor-verbindingen: van ringen tot kooien

Het in dit proefschrift beschreven onderzoek was gericht op het vergroten van de toegang tot (multi)cyclische organofosfor verbindingen. Het inbrengen van fosfor in koolstof frames kan leiden tot verbindingen die o.a. interessant zijn als potentieel ligand voor homogene katalyse of als basis voor nieuwe materialen. Veel verschillende reactietypes en bouwstenen kunnen uiteindelijk leiden tot de nieuwe ring- en kooistructuren. De ontwikkeling van simpele routes naar zulke verbindingen is een nauwelijks onderzocht gebied.

In de *inleiding* geven we een overzicht van literatuuronderzoek dat gerelateerd is aan het werk in dit proefschrift. Daarin komen electrofiele fosfinideen addities naar voren die bijvoorbeeld leiden tot quadraciclane **1** en BABAR-phos **2**.

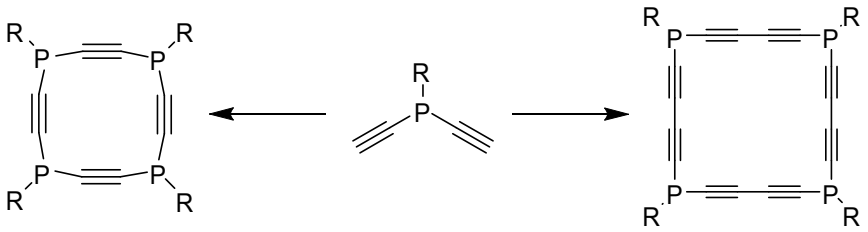


1

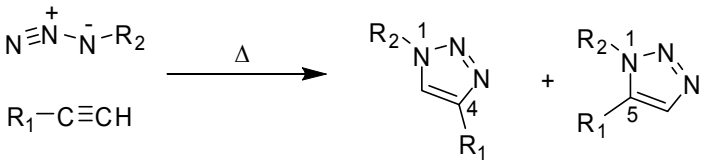


2

Behalve fosfinideenaddities is het ook mogelijk om met behulp van Grignard reacties met halogeen-fosfines of meerdere C-C koppelingsreacties zeer interessante verbindingen te synthetiseren. Ethynylfosfines kunnen voor deze reacties als bouwstenen gebruikt worden.

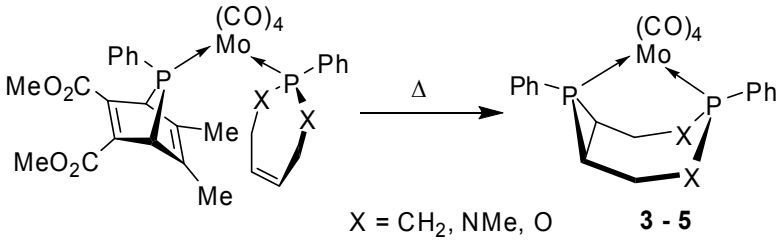


De bouwstenen en cyclische producten zijn interessante startmaterialen voor verdere functionalisatie. Een mogelijkheid is om vanuit de resterende R-substituent 3-dimensionale structuren te maken. Een andere mogelijkheid is het gebruik van de acetyleen groep. Deze is uitermate geschikt voor reacties zoals de Huisgen 1,3-dipolaire cycloadditie met azides.



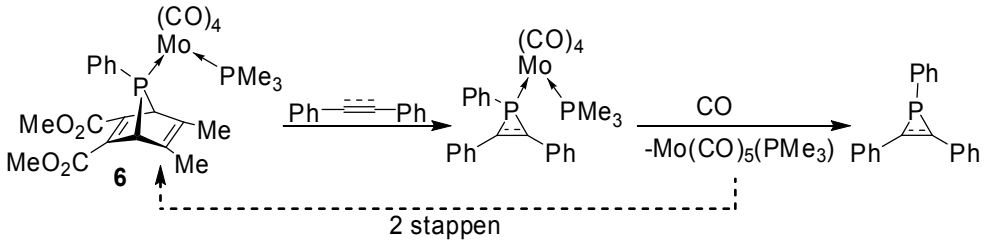
De eerste liganden met een fosfine gesubstitueerd triazole systeem zijn sinds kort bekend. Deze ClickPhos-liganden leverden veelbelovende resultaten in Pd-gekatalyseerde Suzuki-Miyaura koppeling en aminering reacties van arylchlorides.

In *hoofdstuk 2* beschrijven we de synthese van 3 nieuwe bidentaat fosfine Mo-complexen via een *intra*moleculaire fosfinideen additie. Interessant aan deze verbindingen is o.a. de incorporatie van een gespannen fosfiraan ring in deze multicyclische structuur. Verder is aangetoond dat vrij eenvoudig verschillende substituenten rond het 2e fosfor atoom geplaats kunnen worden als uitgegaan wordt van CH_2-, N(Me)- of O-gesubstitueerde fosfepines.



Kristalstructuren geven een gedetailleerd beeld van de N- en O-gesubstitueerde baskets. Ten opzichte van een al bekende basket, gesynthetiseerd via *intra*moleculaire additie aan een fosfoleen ring, is de P-Mo-P hoek wel vergroot van 69° naar 77°, maar deze is relatief klein voor een zes-ring chelaat. Vooral de CH_2 en O gesubstitueerde baskets zijn zeer stabiel. Pogingen tot decomplexatie van deze ligandsystemen zijn tot nu toe vruchteloos gebleken.

In *hoofdstuk 3* hebben we de tot nu toe bekende reacties tot vrije fosfiranen uitgebreid met een nieuwe decomplexatie route. Een nieuwe fosfinideen precursor (**6**) gebaseerd op het 7-fosfanorbornadieen $Mo(CO)_5$-complex is gesynthetiseerd waarbij een *cis*-CO ligand is vervangen door een PMe_3 ligand. Dit resulteert in een verlaging van de temperatuur waarbij het fosfinideen afsplitst van 110 °C naar 70 °C. Additie reacties van het electrofiele fosfinideen complex aan 1,2-difenylacetyleen, 1,2-*trans*-stilbeen en styreen leidt tot de isolatie van fosfireen complex en fosfiraan complexen.

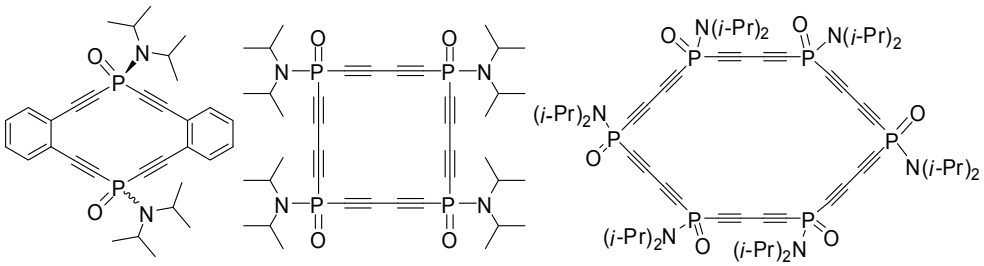


Decomplexatie van de fosfine complexen is eenvoudig te realiseren onder verwarmen op 60 °C en 25 bar CO druk. Daarbij wordt naast de vrije fosfireen en fosfiraan liganden ook $Mo(CO)_5PMe_3$ gevormd wat kan worden hergebruikt in de synthese van het fosfinideen precursor complex.

In *hoofdstuk 4* geven we een gedetailleerd overzicht van onze pogingen om een aantal bouwstenen te synthetiseren waarmee verbindingen met fosfor en acetyleen te maken zijn. De fosfines in dit hoofdstuk zijn geoxideerd zodat de verbindingen makkelijker isoleerbaar zijn. Deze oxidatie is uitgevoerd d.m.v. reactie met ozon. Twee diastereomeren van verbinding **7** zijn geïsoleerd na reactie van $(i\text{Pr})_2NP(O)Br_2$ met gedeprotoneerde 1,2-bisethynylbenzeen, waarvan van de *trans*-isomeer een kristalstructuur is opgenomen. Met ethynylfosfines treedt onder een gelijke omstandigheden een polymerisatie-achtige reactie op. Verbinding **7** is verassend stabiel en decompositie treedt slechts langzaam op boven 300 °C. De amino-groep is te vervangen door een

methoxy-groep na reactie met $BF_3.OEt_2$ in methanol en biedt dus de mogelijkheid tot verder functionalisatie.

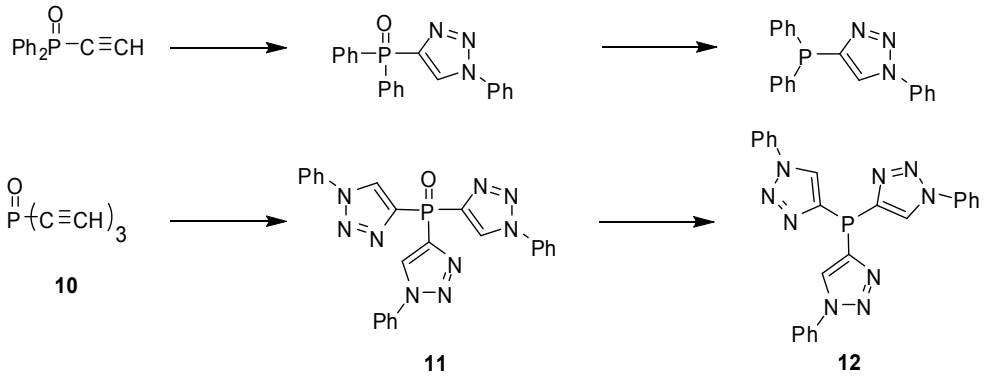
Behalve directe cyclisatie via Grignard reacties kunnen de acetyleen groepen ook gekoppeld worden. Via acetyleen koppelingreacties onder oxidatieve Hay condities (d.w.z CuI, TMEDA, aceton, O_2) kan vrij eenvoudig en in goede opbrengsten een groot aantal nieuwe fosfines met een 1,3-butadiyne linker gemaakt worden. Een directe cyclisatie leidt tot de isolatie van macrocycles **8** (20 ring atomen) en **9** (30 ring atomen) in redelijke opbrengst. Een enkele isomeer van verbinding **9** werd geïsoleerd als 'whisker' (snorhaar), een lange dunne haar-achtige structuur die ook gezien kan worden als een soort van dichte nanotube.



7 **8** **9**

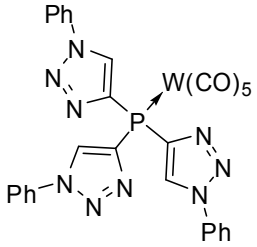
In *hoofdstuk 5* zetten we het onderzoek met acetyleen gesubstitueerde fosfine oxides voort. Een serie van 4 verschillende fosfines (**10**) met 1, 2 of 3 acetyleen substituenten is d.m.v. een Cu(I)-gekatalyseerde 'click'-reactie met fenylazide omgezet in triazole gesubstitueerde fosfines. Deze reactie vindt plaats op kamertemperatuur met $Cu(II)SO_4$ en natrium ascorbaat als Cu(I)-bron in een mengsel van water en *tert*-butanol. De triazole producten kunnen eenvoudig geïsoleerd worden na filtratie of kolom chromatografie in goede opbrengsten tot 74%. Enkel de vorming van de volgens het reactiemechanisme verwachte 1,4-di-gesubstitueerde 1,2,3-triazoles (**11**) wordt waargenomen. De P=O binding van de fosfine oxides **11** kan vervolgens eenvoudig gereduceerd worden met $PhSiH_3$ zodat fosfines **12**

geïsoleerd worden in opbrengsten van 90 tot 94%. Deze fosfines zijn stabiel in vaste vorm, maar oxidatie door lucht vindt zeer langzaam plaats in oplossing.



10 **11** **12**

Met fosfine oxides **11** en fosfines **12** is een serie nieuwe verbindingen gesynthetiseerd waaruit een aantal verschillende metaal complexen gemaakt zijn. Reactie van tristriazole **12** met $W(CO)_5(MeCN)$ levert het verwachte $W(CO)_5$-fosfine complex **13** op, waarvan ook een kristalstructuur is opgenomen. Reactie van **11** met $RhCl_3$ levert een complex (**14**) op waarbij de 3 triazole ringen elk coördineren aan $RhCl_3$ door de N op de 3 positie. Van deze verbinding is ook een kristalstructuur bepaald. Hierbij is duidelijk te zien dat de verbinding een propeller vorm heeft waarbij de 3 fenyl ringen in verschillende mate geroteerd zijn. Interessant is de mogelijkheid om via verbinding **12**, metaal complexen te synthetiseren met 2 verschillende metalen. Een begin is hiermee gemaakt door de reactie van **13** met $FeCl_3$ tot complex **15**.



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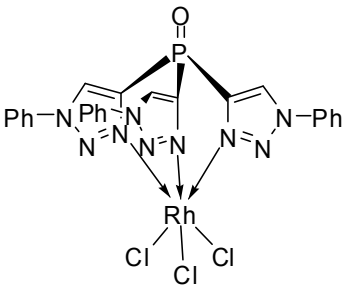

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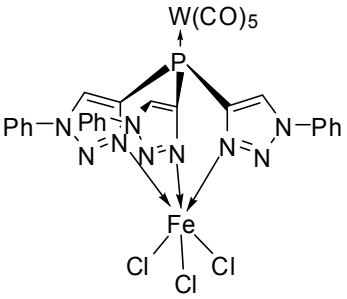
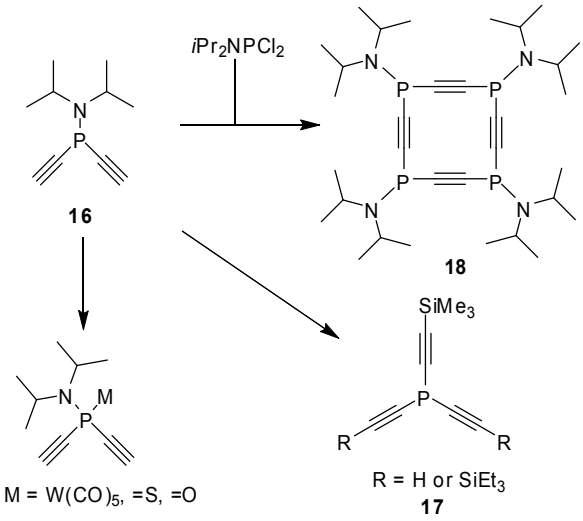


15

In *hoofdstuk 6* gaan we terug naar de ethynylfosfines. De fosfines besproken in dit hoofdstuk zijn echter niet geoxideerd. Het ontbreken van dit stabiliserende atoom uit zich op verscheidene manieren. Fosfine **16** kan gesynthetiseerd worden uit ethynyl magnesium bromide (HC≡CMgBr) en *i*-Pr_2NPCl_2. De amino-groep kan vervolgens gemakkelijk gesubstitueerd worden voor een chloride door reactie met 2 equivalenten HCl-gas en een 2e Grignard reactie geeft een fosfine **17** met verschillend gesubstitueerde acetyleen groepen. Tevens kan dit fosfine na deprotonatie gebruikt worden voor een cyclisatie met *i*-Pr_2NPCl_2 tot fosfapericyclynes **18**.



De combinatie van deze twee eigenschappen lijkt de synthese van 3-dimensionale kooistructuren bestaande uit P en C≡C mogelijk te maken. De gevoeligheid van de ethynylfosfines voor oxidatie maakt de isolatie van de fosfapericyclynes tot op dit moment echter onmogelijk. Indien gewenst kan het fosfor-atoom van **16** beschermd worden door reactie met peroxides tot het oxide, reactie met S_8 tot het sulfide of reactie met $W(CO)_5(MeCN)$ tot het $W(CO)_5$-complex. Reactie met BH_3 geeft een hydroborering van het initieel gevormde boraan-complex.

Afsluitend kan worden geconcludeerd dat er een behoorlijk aantal nieuwe verbindingen zijn gemaakt met P in een ring/kooi omgeving. Via fosfinideen-additities zijn bidentaat fosfiraan liganden dan wel complexen met een verscheidenheid aan andere ring atomen eenvoudig toegankelijk. De mogelijkheid voor decomplexatie van fosfiraan Mo-complexen onder CO-druk opent de weg naar de synthese van andere vrije fosfiranen. De combinatie van acetyleen en fosfor is een lastige. In het geval van P(III) is de isolatie en zuivering van bijv. de fosfapericyclynes een nog te nemen horde. Met fosfine oxides is de synthese van macrocycles uit P en C≡C fragmenten mogelijk door middel van Grignard reacties of oxidatieve Hay koppeling. 'Click'-chemie maakt het geheel af. Een groot scala aan liganden is bereikbaar vanuit de bouwstenen: ethynylfosfine oxides en azide en kunnen gemakkelijk omgezet worden naar metaal complexen d.m.v N-complexatie, P-complexatie, en een combinatie van beiden.

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